

THESIS / THÈSE

DOCTOR OF SCIENCES

**Imidazolium-based heterogeneous catalysts for the conversion of CO₂ into cyclic carbonates
from in-depth understanding of a synergistic activation to enhanced performances**

COMES, ADRIEN

Award date:
2021

Awarding institution:
University of Namur

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Doctoral Thesis

Imidazolium-based heterogeneous catalysts for the conversion of CO₂ into cyclic carbonates: from in-depth understanding of a synergistic activation to enhanced performances

Author:

Adrien COMES

Supervisor:

Prof. Carmela APRILE

A thesis submitted in fulfilment of the requirements for the degree of

Doctor of Sciences

in the

Laboratoire de Chimie des Matériaux Appliqués

Département de Chimie

June 11th 2021

This research used resources of the “Plateforme Technologique Physico-Chemical Characterization” – PC², the SIAM platform (Synthesis, Irradiation & Analysis of Materials) and the MORPHIM platform (Morphology & Imaging) located at the University of Namur.

Examining board:

Prof. Guillaume Berionni (University of Namur, BE)

Dr. Bruno Grignard (University of Liège, BE)

Prof. Paolo P. Pescarmona (University of Groningen, NL)

Prof. Jean-Marie Raquez (University of Mons, BE)

Contents

Contents	3
Abstract	7
Résumé.....	8
Remerciements / Acknowledgements	10
General Introduction	13
Functional Structured Porous Materials	13
Understanding the formation of a porous silica material	14
Functionalization of porous silicates	18
CO ₂ as feedstock	22
Photo-reduction	24
Electro-reduction	25
The direct conversion	26
Catalytic conversion of epoxides to cyclic carbonates: State-of-the-art	29
Green Chemistry	35
Thesis outlines	39
Chapter I Bi-functional heterogeneous catalysts for carbon dioxide conversion: enhanced performances at low temperature	41
Abstract	42
Introduction	43
Results and discussion.....	43
Conclusions	54
Experimental section	55
Materials and methods.....	55
General procedure for the synthesis of SiO ₂ ; Sn-SiO ₂ and Zn-SiO ₂ solids.....	55
Synthesis of SiO ₂ -imi; Sn-SiO ₂ -imi and Zn-SiO ₂ -imi.....	55
Supporting Information	56

Chapter II Multifunctional heterogeneous catalysts highly performing in the conversion of carbon dioxide: mechanistic insights	57
Abstract	58
Introduction	59
Results and Discussion.....	60
Conclusions	73
Experimental	75
Materials and methods.....	75
General procedure for the synthesis of SiO ₂ and Sn-SiO ₂ solids	75
Synthesis of 1-(2-Hydroxypropyl)imidazole.....	75
General procedure for method A functionalization	76
General procedure for method B functionalization	76
Supporting Information	77
Chapter III Imidazolium-based titanosilicate nanospheres as active catalysts in carbon dioxide conversion: towards a cascade reaction from alkenes to cyclic carbonates.....	85
Abstract	86
Introduction	87
Results and discussion.....	87
Conclusions	102
Experimental	104
Materials and Methods	104
Synthesis of Ti-SiO ₂ solids.....	104
Synthesis of Ti-SiO ₂ -imi	104
Catalytic tests: Epoxidation	105
Supporting Information	106
Chapter IV Imidazolium chloride vs magnesium oxide supported on Al_SBA-15 as catalysts for the CO ₂ conversion to cyclic carbonates: on the synergistic activation mechanism	111
Abstract	112

Introduction	113
Results and discussion.....	114
Conclusion.....	125
Experimental	126
Materials and methods.....	126
Catalysts synthesis	127
Supporting Information	129
Chapter V Imidazolium salt and boron Lewis acids supported on silica as heterogeneous bi-functional catalysts.....	131
Abstract	132
Introduction	133
Results and Discussion.....	135
Boron functionalization: initial strategy	135
Boron grafting: new strategy	138
Catalytic tests.....	142
Conclusion.....	145
Experimental	147
Materials and methods.....	147
Synthesis of XS solids	147
Synthesis of XS-Imi.....	147
Synthesis of XS-BP1, XS-BP2 and XS-BP3.....	148
Synthesis of XS-BF1 and XS-BF2	148
Synthesis of 1,3,2-dioxaborolane,4,4,5,5-tetramethyl-2-[2-(trimethoxysilyl)-ethyl].....	148
Synthesis of XS-Bpin and XS-Imi-Bpin	149
Supporting Information	150
General conclusions	153
Future work.....	157

General experimental section.....	159
Materials and Methods	159
N ₂ physisorption	159
Transmission electron microscopy	159
X-Ray diffraction.....	159
Inductively coupled plasma optical emission spectroscopy	159
Combustion chemical analysis	160
Solid-state nuclear magnetic resonance.....	160
Catalytic tests: conversion of epoxides and CO ₂	161
List of abbreviation	163
List of achievement.....	165
Published articles.....	165
Submitted articles.....	165
Articles under preparation.....	165
Master Thesis Supervision	166
Oral Communications	166
Poster Communications.....	167
References.....	169

Abstract

In the context of global warming, the necessity of preserving the environment become more and more leading for people, as well as for industries and companies. In this trend, the Green Chemistry and its 12 principles emerged in the 1980's. These principles are guidelines for chemists to design processes to reduce the use of hazardous and toxic chemicals as well as the production of wastes. Catalysis and the development of new catalysts play a key role to take on these challenges. They allow to decrease the energy barrier of the reaction and increase the reaction speed and/or decrease the reaction temperature. Homogeneous catalysts were developed for years and allowed to perform reactions in a faster way, at lower temperature and some allowed to tackle isomers selectivity issues. But their intrinsic homogeneous usage renders them difficult to recover and to reuse while a heterogeneous catalyst is easily recoverable by filtration or centrifugation and can further be reused for several cycles.

Among the wide range of heterogeneous catalysts, mesoporous silica materials are particularly interesting thanks to the very high specific surface area, their robustness and the wide possibilities of functionalization. It is possible to transform this material in an efficient catalyst through co- and post-functionalization.

In this context, the conversion of CO₂, considered mainly as a waste, is of tremendous interest. In particular, we will focus on the catalytic conversion of CO₂ and epoxides to cyclic carbonates, an attractive class of molecules used in various fields such as batteries (electrolytes) or as precursors of polycarbonates. The synthesis of cyclic carbonates from CO₂ attracted attention of the scientific community as well as industries because safer and greener than the usual strategy using phosgene. Among ionic liquids, imidazolium salts are well known catalysts for this purpose. Their heterogenization on various supports such as surface of polymers, silica, carbon nanostructures or magnetic particles was reported in literature. The attractiveness of imidazolium salts can be reinforced using co-catalysts able to decrease the energy barrier of the reaction. There are only few reports about the heterogenization of both catalyst and co-catalyst on the same support, i.e. a bi-functional material.

The employed strategy in this thesis is the functionalization of a mesoporous silica network by both imidazolium salts and Lewis acid sites, respectively the catalyst and co-catalyst. First, the mesoporous silica network is generated embedding a metal element such as Sn, Zn, Ti or Al as Lewis acid site. Thereafter, the surface is decorated by imidazolium salts. Materials were deeply characterized and a particular interest is dedicated to the Lewis acid site interaction with reactant for the further application in CO₂ conversion.

Résumé

Dans le contexte du réchauffement global et des changements climatiques, la nécessité de préserver l'environnement est devenue une préoccupation majeure du grand public mais aussi des industriels. C'est dans cette dynamique que la Chimie Verte et ses 12 principes sont apparus dans les années 1980. Ces principes sont des lignes directrices pour la mise au point de procédés chimiques qui tendent à réduire l'utilisation de produits dangereux et toxiques ainsi que de minimiser la production de déchets. La catalyse et le développement de catalyseurs jouent un rôle clé pour relever ces défis. Ils permettent de diminuer l'énergie d'activation des réactions et d'augmenter la vitesse et/ou de diminuer la température de réaction. Les catalyseurs en phase homogène sont développés depuis de nombreuses années et permettent d'effectuer des réactions plus rapidement, à plus basse température et certains permettent même de résoudre des problèmes de sélectivité entre isomères. Cependant, leur nature même de catalyseur homogène rend leur recyclage compliqué alors qu'un catalyseur hétérogène est facilement récupérable par filtration ou centrifugation et peut être réutilisé plusieurs fois.

Parmi la large gamme de catalyseurs hétérogènes, les matériaux en silice mésoporeux sont particulièrement intéressants car ils possèdent une haute surface spécifique, une grande robustesse et de nombreuses possibilités de fonctionnalisation. Il est possible de transformer ces matériaux en catalyseurs efficaces par co- ou post-fonctionnalisation.

Dans ce contexte, la conversion du CO₂, considéré comme un déchet, est particulièrement intéressante. Nous nous focaliserons en particulier sur la conversion catalytique du CO₂ et d'époxydes en carbonates cycliques, une classe de molécules utilisées dans des domaines variés tel que les batteries (électrolytes) ou comme base des polycarbonates. La synthèse de carbonates cycliques à partir du CO₂ est attrayante pour la communauté scientifique ainsi que pour les industriels car plus sûre et plus verte que l'utilisation courante de phosgène. Parmi les liquides ioniques, les sels d'imidazolium sont des catalyseurs bien connus pour cette application. Leur hétérogénéisation sur divers supports comme la surface de polymères, de silice, de nanostructures de carbone ou de particules magnétiques a été décrite dans la littérature. L'attrait pour les sels d'imidazolium peut être renforcé grâce à l'utilisation de co-catalyseurs capables d'abaisser encore l'énergie d'activation de la réaction. Cependant, il y a peu d'articles rapportant l'hétérogénéisation à la fois du catalyseur et du co-catalyseur sur le même support, c'est-à-dire la synthèse d'un matériau bifonctionnel.

La stratégie employée dans cette thèse passe par la fonctionnalisation d'un matériau en silice mésoporeux à la fois par un sel d'imidazolium et par un acide de Lewis, respectivement

catalyseur et co-catalyseur. D'abord, un réseau de silice mésoporeux sera synthétisé avec en son sein, un élément métallique tel que de l'étain, du zinc, du titane ou de l'aluminium inséré comme acide de Lewis. Après cela, la surface sera recouverte par des sels d'imidazolium. Les matériaux seront caractérisés complètement et une attention particulière sera portée aux interactions des sites acides de Lewis avec les réactifs pour l'application qui suivra : la conversion du CO₂.

Remerciements / Acknowledgements

Success is not final. Failure is not fatal. It is the courage to continue that counts.

Sir Winston Churchill.

Les prochaines lignes seront en français car je ne pourrais certainement pas trouver les mots justes dans une autre langue que ma langue maternelle pour exprimer ma gratitude pour ces belles années. Me voici donc arrivé au bout d'une longue aventure. Durant ces six années, j'ai certainement énormément progressé et je ressors de cette expérience grandi. Ça n'aurait certainement pas été possible seul et c'est pourquoi ces remerciements me sont chers.

Je tiens tout d'abord à exprimer ma sincère gratitude à ma promotrice de thèse, la Professeure Carmela Aprile. Durant ces années passées dans son laboratoire, j'en ai au moins autant appris sur la chimie que sur moi-même et sur les autres. La rédaction de cette thèse est pour moi l'occasion de remettre en perspective tout ce que j'ai pu apprendre et qui ne se limite certainement pas au laboratoire mais s'étend bien au-delà.

Au moment d'écrire ces remerciements, je suis touché par la confiance qu'elle m'a accordée dans mes prises de décisions et dans la liberté qu'elle m'a accordée pour mener mes recherches. Cette liberté m'a permis d'explorer en profondeur mon sujet de thèse ainsi que de réaliser de nombreuses expériences au-delà de ce projet. Ses mises au point ponctuelles m'ont parfois évité de partir à la dérive dans mes idées, parfois trop entraîné par ma curiosité.

Je suis touché par la confiance accordée lors de l'encadrement de cinq mémoires ; la confiance de ma promotrice ainsi que celle des étudiants. Cela m'a permis de partager directement mon expérience avec eux.

Je suis touché par la confiance accordée pour mener des collaborations avec des groupes de recherches, au sein de l'Université de Namur et en dehors. Cela m'a permis de me découvrir d'autres manières d'envisager la recherche, d'autres manières de procéder.

Je suis touché par la confiance accordée dans le laboratoire vis-à-vis de nombreuses tâches pour pouvoir aider tous les membres de l'équipe.

Tout ce temps passé au laboratoire aurait été certainement bien différent sans la présence de tous ceux qui en font, je le pense sincèrement, un laboratoire exceptionnel. Au moment de le quitter, je ne peux évidemment pas oublier ceux qui le font vivre en ce moment : Alvisé, Alexandra, Loraine, Amélie, Anthony mais aussi Andrea, Alessandra, Hussein et Jennifer. Je pense bien aussi à ceux qui l'ont fait vivre lors de leur passage : Lucia, Valerio, Rémy, Nicolas, Esther, Nicolas, Octave, Chloé, Sandrine et Carla.

Je remercie également les personnes avec qui j'ai pu collaborer directement et qui m'ont offert leur expertise de scientifique dans leurs domaines respectifs : Luca Fusaro, Corry Charlier, Valérie Charles, Pierre Louette, Nikolay Tumanov, M. Giorgia Cutrufello, Sonia Fiorilli. Sans eux, cette thèse serait bien pauvre.

Ces six années de thèse s'étant réalisées dans le cadre de l'assistantat, j'ai aussi eu une belle opportunité d'apprendre aux étudiants depuis la chimie de base jusqu'à l'encadrement de mémoires. Je remercie ici toute l'équipe didactique (particulièrement Isabelle Ravet, Diane Bailleul, Laurence Leherte) qui m'ont fait confiance pour accompagner des étudiants dans un moment de leur cursus universitaire. C'est l'occasion de penser évidemment à tous mes collègues assistants pour tous les bons moments ensemble. Je pense particulièrement à Quentin, Sébastien, Marie, Loïc, Marine, Jérémy, Sarah, Loïc, Pierre et tous ceux qui avec qui j'ai eu l'opportunité de travailler de manière plus ou moins proche.

Je remercie également les membres de mon jury de thèse et de mon comité d'accompagnement pour leurs commentaires et remarques constructifs : Prof. Guillaume Berionni, Dr. Bruno Grignard, Prof. Pierre Louette, Prof. Paolo P. Pescarmona et Prof. Jean-Marie Raquez.

Je ne serais jamais arrivé au point où j'en suis sans le soutien de mes proches, mes amis, ma famille. Merci à tous ceux qui ont cru en moi. Je pense particulièrement à mes parents. Sans leurs valeurs, leur éducation, leur sens de l'effort, leur volonté, jamais je ne serais devenu la personne que je suis aujourd'hui. Ce travail, c'est un peu le leur aussi.

Enfin, Pauline, tu as eu sur moi une influence que tu ne mesures probablement pas. Tu as aussi eu des répercussions sur cette thèse sans peut-être le soupçonner. Sans toi, je ne serais pas la personne que je suis. Sans toi, je ne suis pas sûr que cette thèse aurait pu avoir lieu.

General Introduction

Functional Structured Porous Materials

In the past century, many silica supports and silica-based catalysts were developed thanks to the sol-gel process. The sol-gel approach was largely employed not only for the synthesis of silica-based solids but also for the preparation of metal oxides with various morphologies and textural properties which can find applications in various fields as electronics, opto-electronics, catalysis, photo-catalysis or medicine. Concerning the silica-based materials, one of the most preeminent methods is represented by the synthesis of silicates by hydrolysis and condensation of silicon alkoxides using the Stöber researches.[1]

The sol-gel process has been in the spotlight since 1992 when Mobil published the synthesis of mesoporous materials via a liquid-crystal templating (LCT) mechanism.[2, 3] The regular porous arrangement in the solid is generated via hydrolysis of the silica precursor followed by condensation around an LCT that is removed afterward. Few years later, the discovery of Zhao made another breakthrough in the development of mesoporous materials using non-ionic surfactant.[4] After these pioneer researches, many other materials with tuneable pore size and shape were obtained in the form of powder, mono-block or thin layer.

The mechanism involved in the synthesis of mesoporous silicates was studied in-depth to understand or master the textural and structural properties of the final solids.[5] The generally accepted pathway is the following: amphiphilic molecules are dispersed in a solution and, under appropriate conditions (concentration, temperature, nature of the solvent ...), they will arrange to minimize the interaction of the hydrophobic part and maximize the interaction of the hydrophilic part with the solvent which is usually represented by water. This generates the LCT. Thereafter, a silica precursor (usually a silicon alkoxide) is added to this solution (under acid or basic conditions) and a series of hydrolysis and condensation reactions occur to generate Si-O-Si bonds around the LCT. The final material is recovered by filtration or precipitation and dried. Finally, the surfactant molecules trapped inside the SiO₂ matrix are removed (usually via extraction or thermal treatment) to give a porous and organized structure.

There are many parameters to play with in order to tune the textural properties of the materials. For example, the nature of the template, its concentration, the solvent (only water or mixed with alcohol), the temperature, the reaction time, the addition of a swelling agent or salt should be considered. A more detailed view of the mechanism is presented in the following paragraphs.

Understanding the formation of a porous silica material

Several mechanisms of reaction can be involved in the preparation of a porous silica network in function of the reaction conditions used, mainly the pH and the nature of the surfactant. In order to act as templating agent, an amphiphilic molecule is required. These molecules, also called surfactant are made of a hydrophobic chain and a hydrophilic part. There are various types of surfactants which can be mainly classified as cationic, anionic and neutral. One of the most employed surfactants is represented by the cetyltrimethylammonium bromide (CTAB), depicted in Figure 1. This cationic surfactant can generate micelles due to its amphiphilic properties.

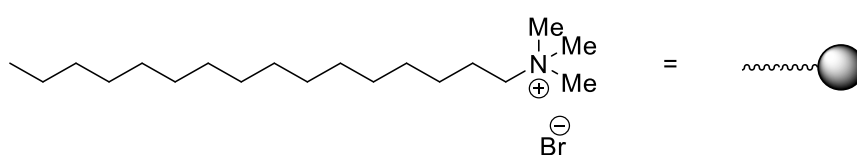


Figure 1: CTAB surfactant molecule

Depending on the concentration in solution, the CTAB molecules tend to form a supramolecular structure via weak van der Waals interactions. At low concentration, these molecules organise at the water-air interface to form a layer. Each carbon chain interacts with others perpendicularly to the liquid-gas interface, on the top layer, while the trimethylammonium group is solvated by the water molecules. Increasing the surfactant concentration, the top layer is full and the CTAB molecules organize in a different way. Therefore, they organise in a spherical shape. These transitions from one arrangement to another is called Critical Micellar Concentration (CMC). Increasing even more the surfactant concentration, the spherical arrangement passes to a tubular one. Then, supramolecular tubes arrange themselves in a hexagonal shape.[6] One of the most known materials obtained employing the CTAB as surfactant is represented by the MCM-41 where the silica is organized around the liquid crystal formed by CTAB.[2, 3]

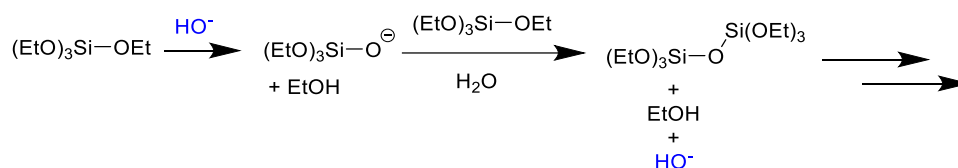
Similarly, anionic, zwitterionic and neutral surfactants may arrange to form micelles. The anionic surfactants may present carboxylate, phosphonate, sulfonate or sulphate moieties covalently connected to a hydrophobic tail.[7, 8] One of the most used in industry is the sodium dodecyl sulphate (SDS) depicted on Figure 2a. The zwitterionic surfactants are constituted of both a positive and a negative charge. As an example, this is achieved by a combination on the same molecule of both an ammonium and a sulfonate like in the myristyl sulfobetaine (Figure 2b). The most used class of non-ionic surfactants is represented by the Pluronic family of surfactants. Among them, the P123 (Figure 2c) which is a co-polymer triblock with two times

a)

b)

c)

Once the LCT is formed, the generation of the SiO₂ network around the micelles may take place. This process occurs through a series of hydrolysis and condensation of a silicon alkoxide such as tetraethylorthosilicate (TEOS) around the preformed surfactant organization. This process can be catalysed by acids or bases. Under alkaline condition, the TEOS is hydrolysed through a nucleophilic attack by a hydroxide anion. The elimination of a molecule of ethanol is assisted by H₂O, leading also to the generation of a siloxide. The resulting siloxide is able to perform a nucleophilic attack on another TEOS molecule which lead to the desired Si-O-Si link with the generation of a molecule of ethanol and the regeneration of the initial hydroxide anion catalyst. This reaction goes on and on, as a polymerisation. This process is depicted on the Figure 3.



Under acidic condition, the TEOS is attacked directly by a water molecule. This is possible thanks to the prior activation by an acidic proton on the TEOS molecule. The generated silanol group attacks another TEOS molecule also activated by the acidity. It generates the Si-O-Si link. Again, the reaction goes on and on, as depicted on the Figure 4.

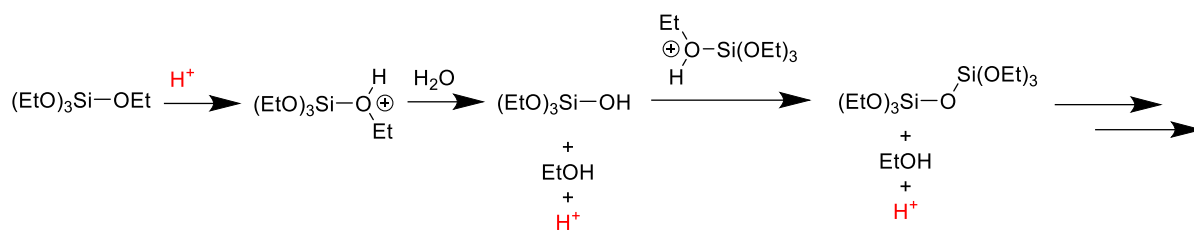


Figure 4: Hydrolysis and condensation of TEOS under acidic condition

The different nature of the inorganic species (cations or anionic) generated in solution under acid or basic conditions and their interaction with the surfactant is one the key point to understand the mechanisms of formation of the silica network with a regular porosity. Under alkaline condition, the silica precursor is negatively charged (I^-) while it is positively charged (I^+) under acidic condition. The different mechanisms are schematized on Figure 5. For instance, in the specific case of MCM-41, the reaction is performed under alkaline condition in order to ensure the electrostatic interaction between the I^- and the positively charged CTAB surfactant (S^+).^[5] Nevertheless, it is still possible to perform the synthesis around the CTAB organizations under acidic condition. This second approach requires a counterion (X^-) such as Cl^- or Br^- to mitigate the $\text{I}^+ \text{S}^+$ repulsion.^[9] El Hankari further developed the concept using a zwitterionic precursor $((\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2)_3\text{N}^+\text{CH}_2\text{CH}_2\text{SO}_3^-$ where the I^+ directly anchored to a sulfonate moiety interacts strongly with CTAB (S^+).^[10]

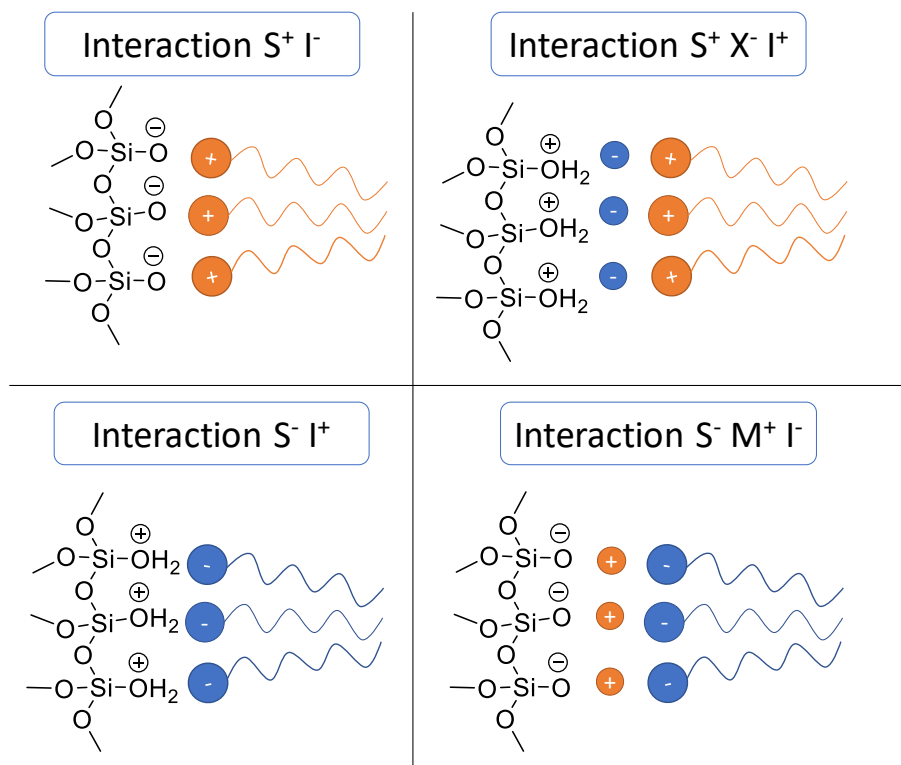


Figure 5: Representation of the various interactions between the surfactant and the inorganic species

Interestingly, the synthesis of materials using S^- such as SDS (sodium dodecyl sulphate) under acidic condition (I^+) does not lead to the formation of any material. This behaviour could be ascribed to the too high isoelectric point of sulphate function. To circumvent this issue, the aminopropyltriethoxysilane (APTES) can be used in combination with TEOS. Under mild acidic condition, the ammonium generate a coulombic interaction strong enough with the SDS to arrange the SiO_2 . This was discovered in 2003 by Tatsumi and it was applied to the synthesis of various materials.[7, 8, 11, 12]

As mentioned previously, in 1998, Zhao opened the door to the use of non-ionic surfactant such as P123.[4] In this case, the interaction between the inorganic species and the surfactant does not occur through a direct ionic interaction. The interaction is mitigated by a $S^0H^+X^-I^+$ under acidic condition. The polyethylene oxide chains are partially protonated as well as the inorganic species I^+ . It is the X^- that plays the role of mediator between the positive charges' repulsion. The use of P123 does not only generate the desired mesoporosity. Additionally, to the mesopores, the SBA-15 materials, as well as other materials synthesized using Pluronic surfactants, are made of interconnected micropores as a result of the presence of the end-chains from the P123 surfactant which are perpendicularly oriented to the direction of the tube. The presence of micropores was proven by N_2 physisorption and by a reverse templating synthesis.[13] The porous matrix was impregnated with carbon and the silica was removed using HF. The resulting carbon structure retains the regular arrangement of the pores. The carbon tubes are interconnected by microtubes originally the micropores from the silica. [14]

From what described previously, the choice of the surfactant will have a direct influence on the porous organization and pore size distribution of the final solid. However, the size of the tubular arrangement can be also tuned with the introduction of a swelling agent such as mesitylene or toluene.[15] These apolar molecules are not miscible with the water solution. On the contrary, these swelling agents tend to interact with the apolar tail of the amphiphilic surfactant. As the surfactant was already organized with a tubular arrangement, the presence of toluene or mesitylene in the core of the tube increases its diameter.

There are then many parameters to play with in order to tune the textural properties of the materials. The nature of the surfactant, its concentration or the presence of a swelling agent were already mentioned. There is also the reaction temperature, time, the solvent employed or even the silicon alkoxide used. Recently, it has been proved that the concentration and nature of the base in solution was a key parameter to control the overall size of the mesoporous particles. It was demonstrated that silica particles of reduced size (lower than 100 nm) display reduced diffusion limitations that analogous silica solids with standard particle size (superior

to 300 nm). Moreover, a direct correlation between size and catalytic activity was found with the silica-based particles of smaller size displaying the higher catalytic performances.[1, 16-19] Investigation by TEM, N₂ physisorption as well as low-angle XRD revealed this correlation and the possibility to control the size from 50 to 200 nm. These extra-small particles (XS) are particularly interesting for the catalysis to enhance the diffusion of the reactants and the products in the porous structure.

After a potential ageing, filtration of the gel and drying, the template must be removed to free the porous space. There are various ways to proceed in order to remove the surfactant. The most common is the calcination at high temperature (450-550 °C) under air. The high temperature ensures a complete condensation of the silanol groups of the material as well as a complete degradation by combustion of the organic template. This thermal treatment is sometimes performed under nitrogen/air or argon/air atmosphere when the presence of oxygen in high concentration could have a detrimental effect on the preservation of the final porous architecture or could promote some sintering phenomena. In these cases it can be suitable to perform an increase of the temperature under inert atmosphere prior to a complete combustion under air.[20] The first step under nitrogen allows the structure to stabilize prior to the removal of the template by combustion under oxygen. The template can also be removed by solvent extraction. The material can be immersed in an organic solvent for several hours under agitation to allow the complete removal of the surfactant that is solubilized and washed off. A similar but more thorough manner to proceed is to wash the material with a Soxhlet apparatus. The use of ozone and UV light is rarer but presents some advantages when the other methods must be avoided and/or are inefficient.[21] On the counterpart, it generates a toxic gas and is very long procedure. This is a niche technic only used for samples and hardly adaptable to large scales.

Functionalization of porous silicates

The applications of pure mesoporous silica structure as MCM-41 or SBA-15 can be widened through various type of functionalization. Here, the functionalization strategies are divided in two main classes: the co-synthesis and the post-functionalization.

Functionalization by co-synthesis

In the co-synthesis, the desired precursor, either organic or inorganic, is mixed with the silicon alkoxide in the sol. This approach is largely employed to achieve the insertion of hetero-elements (with hetero different from silicon) in the silica structure via isomorphic substitution of silicon with a metal cation. For instance, to introduce a hetero-element such as aluminium,

gallium or tin, the corresponding salt is dissolved in alcohol and added to the sol together (or even premixed) with TEOS, the most commonly employed silicon alkoxide. These hetero-elements will be inserted within the silica architecture during the hydrolysis-condensation process. Alternatively, some elements can be inserted as single-site by adding the corresponding alkoxide to the reaction mixture. Titanium isopropoxide or butoxide are often used to prepare titano-silicates since the corresponding titanium chloride is highly reactive. Indeed, the use of the last precursor would lead to segregation of titania and silica instead of the desired insertion of titanium as single site. On the counterpart, some other metal salts are less reactive, e.g. gallium nitrate or tin chloride. They can be used as precursors to lead to the insertion of gallium or tin as single-site. The co-synthesis strategy often ensures a homogeneous dispersion of the hetero-element within the silica matrix.

The integration of metal oxide nanoparticles in the silica structure can be also achieved via co-synthesis. The objective is generally to stabilize the nanoparticles and avoid their sintering while preserving their accessibility through the porous silica network. Nanoparticles are usually prepared prior to an integration in the walls of the silica. An example is represented by TiO_2 or ZnO nanoparticles which were efficiently integrated in various silica structures. [20, 22] Noble metal nanoparticles such as Pd or Au were also used. [23, 24]

Organic functionalization is also possible via a co-synthesis strategy employing various trialkoxysilane-based organic moieties. One example is represented by the tuning of the hydrophilic-hydrophobic balance of the silica surface achieved using a mix of TEOS and methyltriethoxysilane ($\text{MeSi}(\text{OMe})_3$) in the reaction mixture.[25-27] The main challenge of such a synthesis is the temperature of calcination that must be high enough to remove effectively the template while preserving the alkyl functionalities of the surface.[25] Other trialkoxysilanes with propyl ($\text{PrSi}(\text{OR})_3$),[28] phenyl ($\text{PhSi}(\text{OR})_3$),[28] or trifluoromethyl ($\text{CF}_3\text{Si}(\text{OR})_3$) [29] groups were also used with the same purpose. The homogeneous incorporation of organic moieties in the silica framework can also be achieved using various bridged triethoxysilane [30-32] as represented in Figure 6. The bridging moieties can be also modified after their integration in the material. A vinyl group can be for example post-functionalized (e.g. via thiol-ene reaction) or oxidized to give the corresponding epoxide. The bridging moieties can also be used as anchoring point for the heterogenization of a more complex structure.[31]

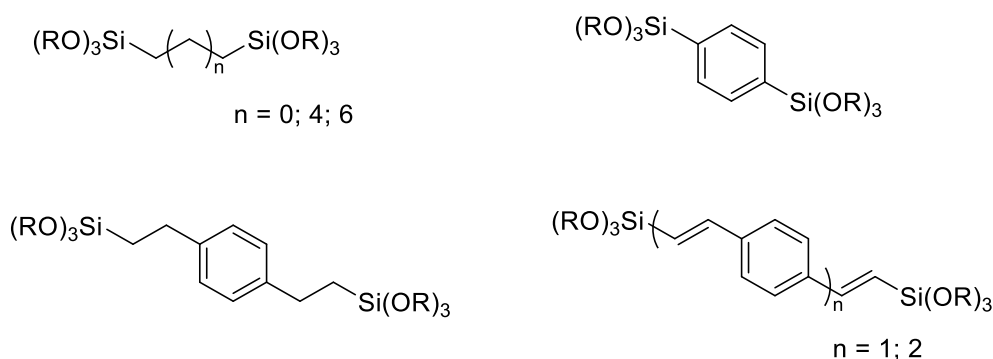


Figure 6: Bridged trialkoxysilanes

Interestingly, various structures have been synthesized including an ionic liquid as bridging moieties (Figure 7).[24, 33-36] In 2004, Baleizao designed a complex of vanadium with trimethoxysilane on both terminations. By co-synthesis, the complex is integrated in a silica network and the resulting solid was used as heterogeneous catalyst.[37] The vanadium complex can be synthesized using a classical pathway and heterogenized in the last synthesis step.

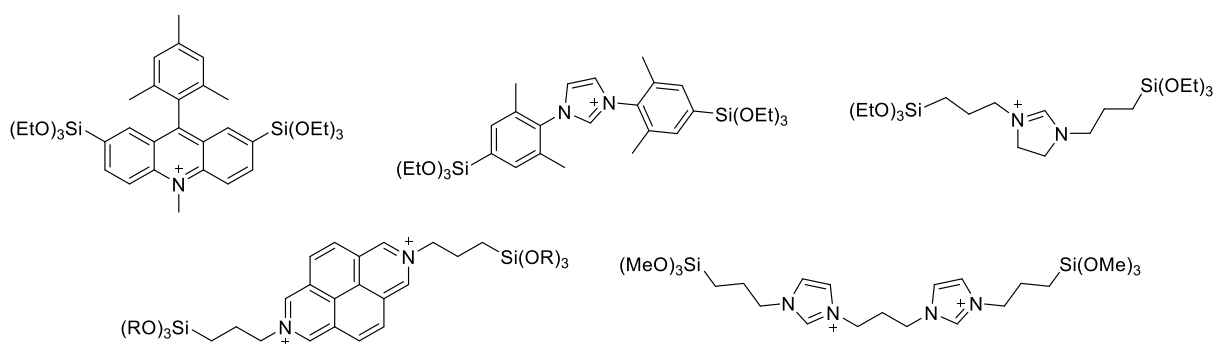


Figure 7: Ionic liquid as bridging trialkoxysilane

The co-synthesis presents the advantage to disperse homogeneously the functional moieties, either organic or inorganic, within the silica matrix. Conversely, the dispersion occurs also in the wall. Hence part of the active species is inaccessible which is a drawback for catalytic applications. Nevertheless, since pioneering work of Tatsumi, [7, 11, 38] it was demonstrated that a careful selection of the surfactant may favour the dispersion at the silica surface thanks to a surfactant-precursor ionic interaction. [8, 12]

In addition, the modification of the sol, via addition of a metal salt or a different alkoxy silane, modifies the synthesis parameters often leading to modification of the textural properties of the material.[19] This means that the condition of the synthesis must be adapted and optimized.

Post-functionalization

In post-functionalization, the mesoporous silica is considered as a support. This approach is very convenient since the synthesis of various mesoporous silica structures is well mastered. The functionalization occurs thereafter through chemical reaction with the silanols on the

surface of the solid with both organic or inorganic species. For inorganic species, one way to achieve this goal is proceeding via incipient wetness impregnation. The material is immersed in a solution of a metal salt and the evaporation of the solvent forces the cations and anions of the salt to go in the pores. After impregnation, some metal precursor like Au, Pd, Pt can be reduced to the metallic state to produce metal nanoparticles. Some of the most used reducing agents are NaBH_4 or LiAlH_4 . In addition, reduction can be achieved under a H_2 stream at high temperature. One challenge of this method is the control of the dispersion on the surface as well as the control on the particles size.

The incipient wetness impregnation is applied likewise to other metal such as Sn or Ga to anchor the hetero-element as a single site. The salt, again, enters in the porous silica and a thermal treatment fixed irreversibly the Sn or Ga by a condensation reaction with surface silanol. Recently, some researchers used complexing agent like citrate, lactate or acetylacetonate to enhance the dispersion of the metallic element on the surface, leading to single sites instead of undesired nanoparticles.[39-43]

The use of organosilanes is also a common approach to functionalise the surface of the silica. All previously described molecules in the co-synthesis part can be used also in the post functionalization. For example, the hydrophilic-hydrophobic balance of the silica surface can be tuned using methyltriethoxysilane [26, 44] as well as propyltriethoxysilane,[45] phenyltriethoxysilane,[45] cyclohexyltriethoxysilane or fluorotriethoxysilane.[28]

To go further in the functionalization, the surface can be modified with a linker displaying a trialkoxysilane functionality and a reactive coupling group which can be used to anchor the desired organic moiety. Some of these coupling reactions are represented in Figure 8. The 3-(mercaptopropyl)trimethoxysilane is commonly used as linker to be anchored at the surface for a further functionalization through the thiol-ene coupling. [46-48] The same strategy is used with 3-(aminopropyl)triethoxysilane [49, 50] that is used as anchor through the generation of an amide group, mimicking the peptide synthesis developed by Merrifield.[51] The same kind of application was performed with 3-(chloropropyl)trimethoxysilane (in this thesis) or 3-glycidyloxypropylsilane [52-56] that can act as electrophiles with respectively the leaving of chloride anion or the 3-member ring opening. These open a large field for various functionalization by organic molecules.

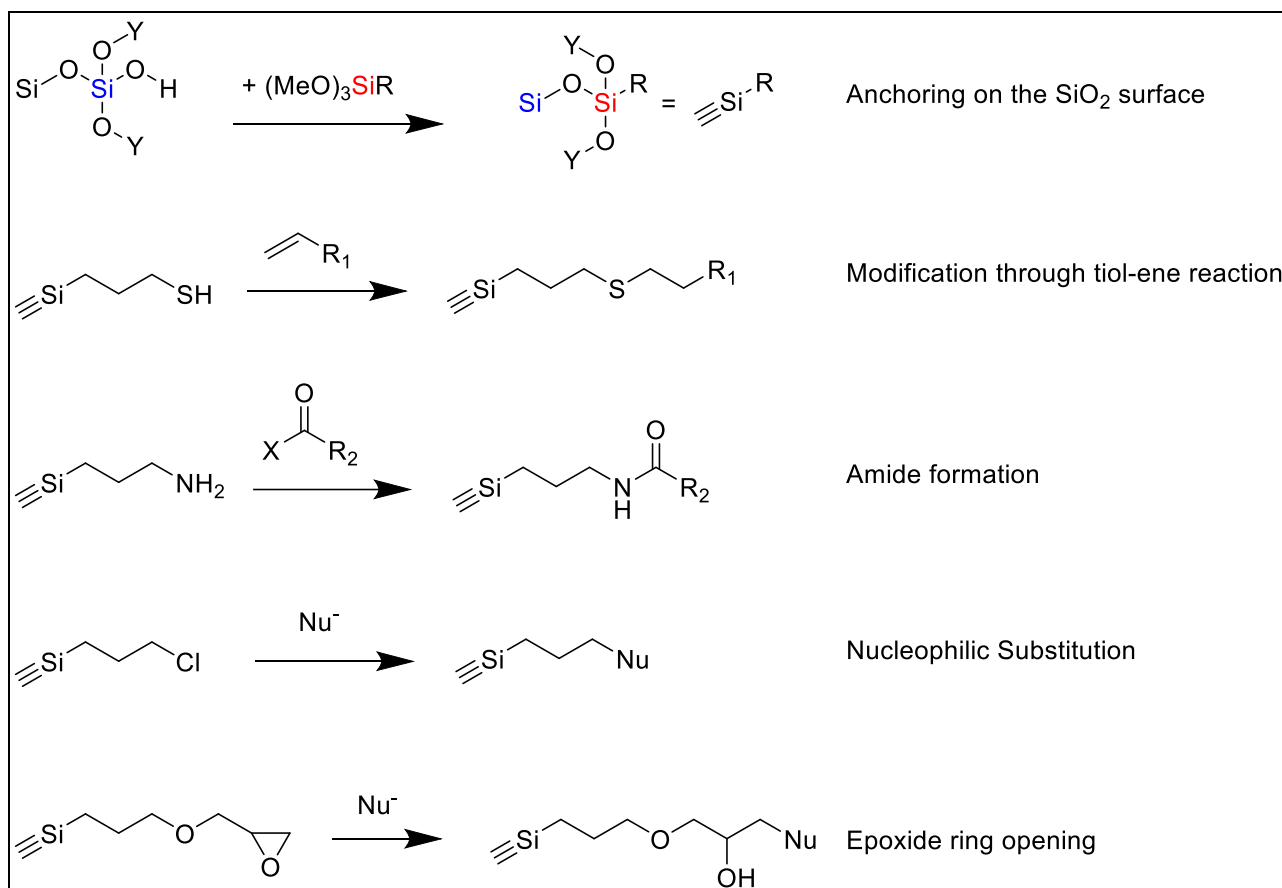


Figure 8: Anchoring of linker on the silica surface and several coupling reactions. Y stands for Si or H. Nu⁻ stands for nucleophile. X is a leaving group.

CO₂ as feedstock

The functionalized porous materials described in the previous sections can find application in various fields in chemistry from large scale industrial processes to small scale specialized high-value chemicals synthesis.

The last report from IPCC (Intergovernmental Panel on Climate Change) alarms once again people about the impacts of climate change. Scientists stated clearly the direct link between human activities, exploitation of fossil fuels and carbon dioxide (CO₂) emissions as cause of the greenhouse effect leading to the global warming and the climate change.[57] Carbon dioxide increase corresponds to the beginning of the Industrial Revolution. The most used tool to assess the increase of this gas in the atmosphere is the Keeling curve and via the measurements performed in Mauna Loa, Hawaii.[58-60] It is important to mention that since 1959, about 45 % of the carbon dioxide released from fossil fuels is not absorbed by lands and oceans and remains in the atmosphere.[61] The stable level of CO₂ in the atmosphere of 260 ppm at the beginning of the 19th century (before the Industrial Revolution) increased constantly to reach 400 ppm in the 2018 (Figure 9).

CO₂ in the atmosphere and annual emissions (1750-2019)

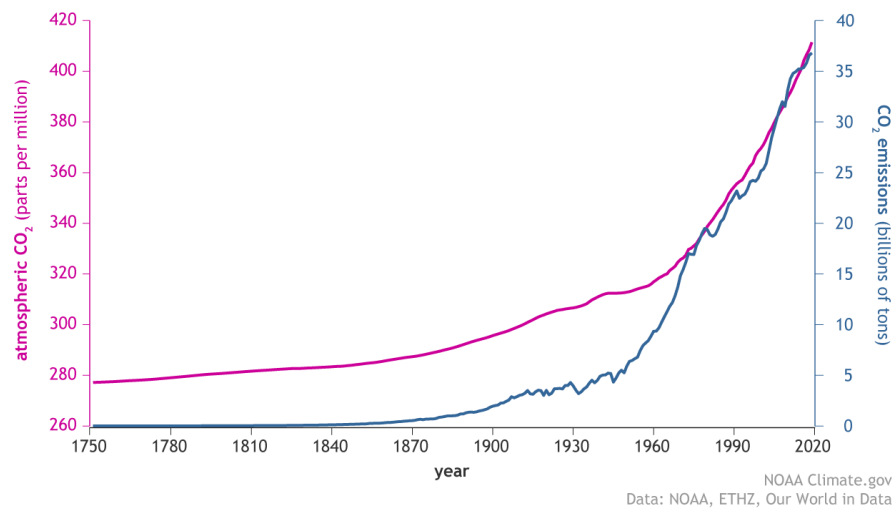


Figure 9: CO₂ in the atmosphere and annual emissions (1750 – 2019)

Humankind faces a global challenge to reduce the carbon dioxide concentration in the atmosphere in order to limit the global warming below 2 °C relative to pre-industrial levels with a long-term objective of a zero emissions of CO₂. [57] The most evident solution is the reduction of fossil fuels utilization. The development of new technologies to preserve the energy and the resources of the Earth is one of the key pillars of the scientific community. [62, 63]

Carbon capture and storage (CCS) constitutes one of the envisaged routes to reduce the presence of CO₂ in the atmosphere. This technology requires the capture and purification of CO₂ [64] and its storage in geological formations or in ocean. However, recent studies [65] demonstrated that the latest approach would cause high mortality of ocean organisms. Hence, the strategy of storage in geological formations remains the most indicate to mitigate the climate change. As drawback, this solution requires additional energy input and long-terms studies over several decades or centuries to analyse the evolution of the situation since it could present leakage risks. [65-67]

Another possibility is to use the physicochemical properties of CO₂ to envisage its direct use. [68, 69] Carbon dioxide is gaseous at ambient pressure and temperature. Its thermodynamic properties are notably used in fridges and cooling systems. It replaced efficiently CFC (chloro-fluoro-carbons) that have very detrimental effects on the ozone layer in the atmosphere. It can be turned from gas to a solid by sublimation allowing to cool processes at -78 °C. This is interesting in transportation and storage of samples since it does not melt and so does not require impervious containers. [70] The recent COVID-19 crisis and the necessity to transport vaccine at least at -70 °C put this utilization under the spotlight. Over 73.8 bar and 31 °C,

carbon dioxide behaves as supercritical fluid. This state of matter is used in various chemical processes such as the extraction or as solvent.[69, 71] This solvent is used for various chemical reactions like hydrogenation, synthesis of organometallic compounds, metal chelation and extraction, preparation of inorganic nanoparticles, polymerization, and even for free radical reactions.[70, 72]

The previously described applications of the carbon dioxide are based on its direct use. To go further, chemists are interested in performing chemical conversion of the CO₂ molecule itself. Chemical transformations of CO₂ are challenging if the high stability of this molecule (standard enthalpy of formation = -393.52 kJ/mol) is considered. Nevertheless, history of chemistry reminds us that nitrogen (N₂) is also a very stable molecule and it is still used for the Haber-Bosch reaction to produce ammonia (NH₃) for decades.[73] Natural systems are able to synthesize molecules starting from CO₂. The best example is given by plants and bacteria that are able to photosynthesize a huge variety of complex structures using CO₂ as feedstock. This process is already exploited in farms for various production[74] from fine chemicals[75, 76] to raw materials such as ethanol,[77] alkanes,[78] and other biofuels.[79-81].

The utilization of plants as a source for chemicals is sometimes thought as a reservoir for industries. But we must be careful that our needs for energies and chemicals to do not compete with croplands and virgin forests.[82] We must remember at this point how important they are in tackling the global warming issue by absorption of the CO₂.

Many other processes are under development to convert the carbon dioxide. Here, it is chosen to divide them in 3 categories: the photo-reduction, the electro-reduction and the direct conversion.

Photo-reduction

The photo-reduction is bio-inspired by natural systems. It is sometimes called the artificial photo-synthesis. The idea is to use the energy of the light to convert the stable CO₂ into valuable chemicals of higher energy. It is desirable to use directly the power of the sunlight since the estimated energy received on the planet in one hour could cover the whole energy needs of humanity for one year.[83-86] In laboratory, even when the process is performed using deep UV-lamps, it still requires less energy than a thermal activation. [86] In any case the use of a photocatalyst (organic, inorganic or hybrid semiconductor) is required. The proposed mechanism is based on the photoexcitation of the semiconductor followed by a charge separation to generate the hole-electron pair. The available electron is then used to reduce the CO₂. [84]

Very recent researches, demonstrated the elevated potential of an iron-containing porphyrin to photo-reduce CO_2 to CH_4 under-visible light, as depicted on Figure 10.[87] Similarly, a Periodic Mesoporous Silica (PMO) material containing biphenyl bridges in the wall was synthesized to harvest the light. A Re-based bipyridine complex was anchored in the pores of the PMO as catalyst to reduce carbon dioxide to monoxide. [88]

These technologies present the potential to create a circular economy. Valuable chemicals are consumed, for instance burned. The generated CO_2 would be collected and thereafter photo-reduced back into a valuable chemical thanks to the solar energy.

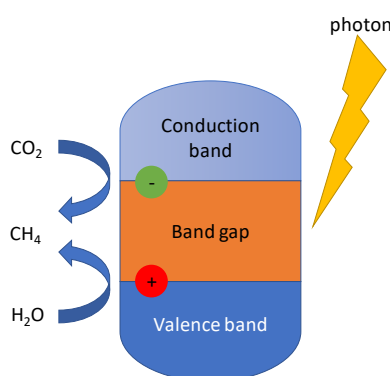


Figure 10: Photoreduction of CO_2 to CH_4

Electro-reduction

Instead of using the light to generate a photo-excited electron, there is a more straightforward mechanism to use: the electro-reduction. This process implies the direct use of electricity to perform a chemical reaction as schematized on Figure 11.

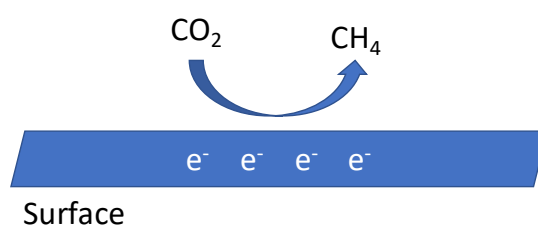


Figure 11: Electro-reduction of CO_2 to CH_4 on surface

This transformation requires the design of new catalysts which are also able to conduct the current. Various examples, were already reported in the literature. Different metals such as copper functionalised with Pd were employed to produce CO, methane, ethylene or ethanol.[89] The use of Ag-based system was described to produce CO, formate, ethanol or ethylene.[90] Gold was employed to produce CO.[91] Recently, new catalysts have emerged thanks to the conductive properties of carbon nanotubes (CNTs). These CNTs-based catalysts were used to produce very selectively methanol thanks to an efficient transfer of multiple

electron mechanism.[92] Nanospikes were also reported for the production of ethanol.[93] New electrocatalysts are then not limited to the reduction of CO₂ to one-carbon containing molecules. Interestingly, the CO dimerization on copper nanoforms open the avenue to coupling reaction to produce ethanol, propanol or ethylene.[90, 94]

The processes of electro-reduction are more and more developed since the production of electricity from renewable sources become prominent to substitute the energy production by fossils. It is advantageous as a mean to store and level the electrical energy produced by intermittent sources such as wind or solar.[95, 96] Nevertheless, it does not appear as a solution to all problems and it must probably be integrated as part of a larger panel of technical possibilities. A recent review demonstrated the interest of combining thermo- and electrocatalysis.[97]

The direct conversion

Carbon dioxide can be converted to valuable chemicals reacting with high-energy molecules such as H₂. The hydrogenation remains the classical way to reduce the most oxidised form of carbon, i.e. CO₂. The high energy molecule H₂ counterbalances the thermodynamic stability of CO₂, making possible the reaction. For several years, scientists were devoted to the production of fuels by catalytic hydrogenation of CO₂ to methane (CH₄), formaldehyde (HCOH) or formic acid (HCO₂H). More advanced catalytic processes allow the conversion to alkanes,[98, 99] aromatics [100] or methanol.[101]

The Sabatier process converts directly the most oxidized CO₂ to the most reduced CH₄ with water as by-product. This reaction is exothermic (-164 kJ/mol). Biological methanation is performed at relatively low temperature (<70 °C) while the corresponding catalytic route requires higher temperature usually c.a. 250 °C. During the process, the production of carbon monoxide as by-product may occur which is reduced also to CH₄. The CO is not an intermediate but a by-product which can be – by Fischer-Tropsch reaction – converted to other useful liquid hydrocarbons. The mechanism of the reaction is strongly influenced by the metal used which are usually Ru, Ir, Rh, Ni, Co. They are often supported on alumina, silica or titania.[102] Methanol production for instance on a Cu/ZnO/Al₂O₃ catalyst is direct at low temperature but is mediated by CO at higher temperature (>260 °C).[103]

To go further, new catalysts based on copper catalysis and more recently on Pd-Cu, Pd-Zn or In₂O were developed to produce more selectively alcohols with longer chains by C-C coupling. This catalysis to produce heavier alcohols is very interesting to generate liquid carbon-neutral fuels using dihydrogen produced from water electrolysis.[104] To be consistent with

sustainability, the hydrogen should be produced by electrolysis of water using electricity from renewables or using emerging techniques. But so far, this is not economically viable compared to steam methane reforming.[105, 106] The direct use of hydrogen presents other drawbacks such as the difficulty of stocking, transporting or safety.[105] These difficulties with dihydrogen could be by-passed if it is used on site to produce these carbon-neutral fuels.

There are various other high energy molecules than hydrogen that can be used as building block to react with the very stable carbon dioxide and produce valuable products.[107, 108] It started in 1922 with the development of the Bosch-Meiser process (Figure 12) to produce urea from carbon dioxide and ammonia.[109, 110] The urea is mainly used for agriculture as fertilizer.

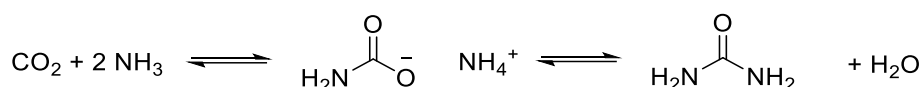


Figure 12: Bosch-Meiser process

Carboxylic acids can be produced by coupling with Grignard (Figure 13) or organolithium reagent (Figure 14), themselves generated from an alkyl or aryl halide. The reaction is rapid and straightforward since it can even work with dry ice, i.e. solid CO₂ at -78 °C, even if limitations related to the high reactivity of organolithium must be taken into account limiting the upscaling for instance.[68] The synthesis of aspirin is also performed by reaction of phenolate and CO₂ to produce the salicylic acid intermediate since 1890 (Figure 15).[111, 112]

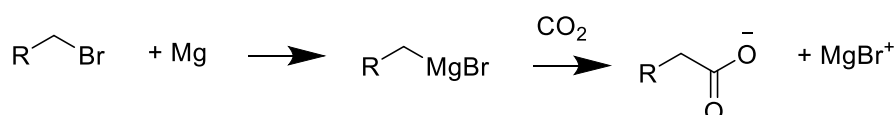


Figure 13: Carboxylate synthesis from Grignard

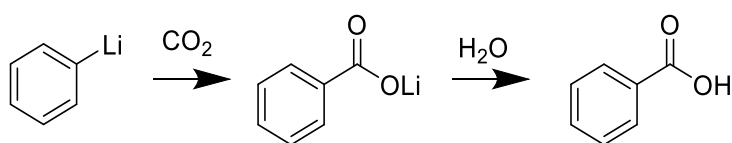


Figure 14: Carboxylic acid synthesis from organolithium

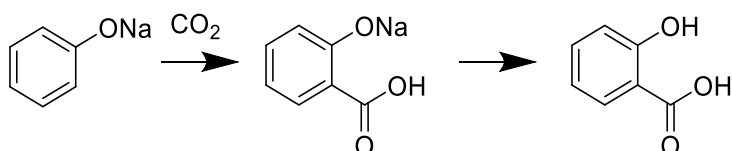


Figure 15: Salicylic acid synthesis from phenolate

In this thesis the focus is on the conversion of epoxides into cyclic carbonates. Cyclic carbonates have various utilization in industry as polymer precursors [113] or as solvents for batteries.[114, 115] This pathway also presents the advantage to avoid the classical route

involving the use of phosgene – a very toxic reagent – and the by-production of hydrochloric acid as demonstrated in Figure 16.[116] About the synthesis of polycarbonates, the use of dimethylcarbonate or cyclic carbonates of large ring size (>5 membered) as carbonyl source is also reported but the process can be claimed as environmental friendly only if the precursors are not produced using phosgene (or another highly toxic or corrosive species) as initial carbonyl source.[117]

The anionic ring-opening behaviour of the cyclic carbonates is known to depend on the ring size. Six-membered cycles (or larger) using anionic initiators tend to polymerize at a relatively low temperature (<100 °C) whilst the polymerization of the five-membered ring is thermodynamically unfavourable and proceeds at a higher temperature (>150 °C) causing the elimination of CO₂ to produce a copolymer that consists of both carbonate and ether linkage.[118]

A direct conversion of CO₂ and epoxides to the polymer is also envisaged in literature. These polymers are produced when the final step of 5-membered ring closure by back-biting is unfavoured compared to the chain propagation. A careful choice of the catalyst as well as the reaction conditions enables to orient the reaction through the production of cyclic carbonates or polycarbonates and eventually to control the polymer structure. The final polymer can be constituted by mixed chains with polyether and polycarbonates resulting from the direct polymerization of the epoxide and insertion of CO₂ in the chain right after the 3-member ring opening.[119] The mechanism involves notably a higher content in Lewis acid site favouring the chain propagation instead of the ring-closure as detailed in the next section.

Some authors, also reported the use of aziridines (instead of epoxides) to produce the corresponding oxazolidines (Figure 17).[120]

Considering the high potential of the cyclic carbonates but the intrinsic limitations of the synthesis of 6-membered rings from oxetane, we will mainly focus on the synthesis of 5-membered ring cyclic carbonates from epoxides.

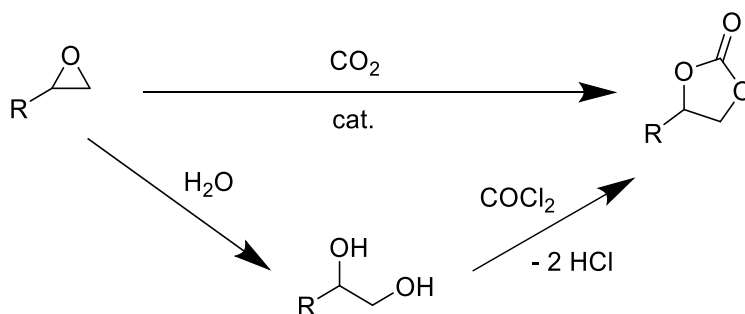


Figure 16: Direct synthesis of cyclic carbonates from epoxides (up) and phosgene pathway (bottom)

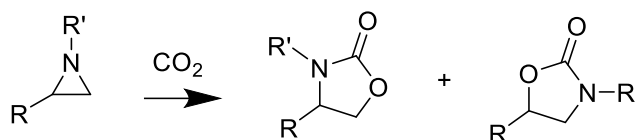


Figure 17: Oxazolidines synthesis from aziridines

Catalytic conversion of epoxides to cyclic carbonates: State-of-the-art

First attempts of coupling epoxides and CO_2 were performed using the 2,3-epoxypropyl phenyl ether as substrate and several salts were tested.[121] It was demonstrated the NaBr and LiBr were the bests catalysts of the series. A first mechanism was already proposed and is still used nowadays. This mechanism is depicted on Figure 18 and involves the initial epoxide-ring opening (1) by a nucleophile (usually the counterion of the salt). The generated alcoholate (b) is a nucleophilic moiety able to attack the electrophilic carbon of CO_2 (2). The catalytic cycle ends with the 5-member ring closure to form the cyclic carbonate and the regeneration of the initial nucleophile (3). The nucleophile is the central moieties since it is responsible of the opening of the epoxide at the step (1) and it acts as leaving group at the step (3). The order of nucleophilicity $\text{Cl}^- < \text{Br}^- < \text{I}^-$ is in agreement with the experimental data and the kinetic of reaction determined by the step (1). On the contrary, fluorine F^- shows almost no activity, probably due its bad leaving group ability at the latest step of the cycle. These assumptions are supported by recent studies using bifunctional porphyrin with various anions and cations.[122]

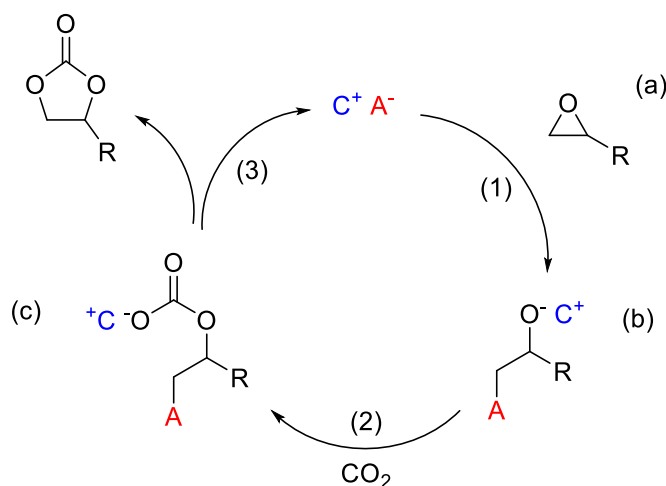


Figure 18: Catalytic cycle for the carbon dioxide conversion with epoxides to cyclic carbonate using ionic liquid (C^+A^-). Path A

A second mechanism was also depicted in Figure 19. This is more probable under high pressure, i.e. when the amount of carbon dioxide is elevated and then more probable to react

with the anion. The CO₂ is directly attacked by the nucleophilic anion to form a carbonate after step (1). This weak nucleophile is able to open the epoxide at step (2). Finally, the ring closure occurs and lead to the cyclic carbonate and the regeneration of the salt.

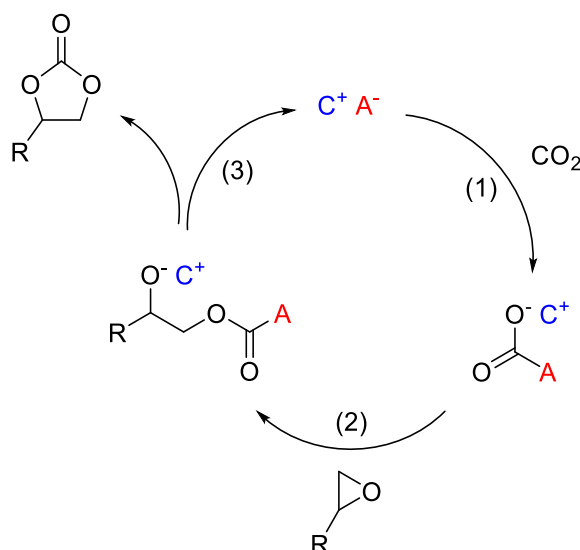


Figure 19: Catalytic cycle for the carbon dioxide conversion with epoxides to cyclic carbonate using ionic liquid (C⁺A⁻). Path B

Recent works from Ema et al. as well as Muller et al. demonstrated via a D-labelled pure enantiomer that the path A (Figure 18) was the most favourable.[122-124] The same group synthesized successfully a new chiral catalyst based on porphyrin to produce in an enantioselective way the desired cyclic carbonate further supporting the prominence of the path A. [125] This enantioselectivity also demonstrates the very efficient activation through the oxygen of the epoxide by the porphyrin.

The recent researches do not rely on the LiBr or NaBr as the pioneering work but on ionic liquids such as ammonium, phosphonium, imidazolium, pyridinium or triazolium salts (Figure 20).[112, 126-128] According to the Hard-Soft Acid-Base theory (HSAB),[129] it worth to use a soft cation such as the aromatic imidazolium with the positive charge delocalized in the 5-membered ring. This renders the hard chloride or bromide anion more available to proceed to the nucleophilic attack compared to the homologue KBr or KCl. It acts as the driving force of the initial nucleophilic attack.

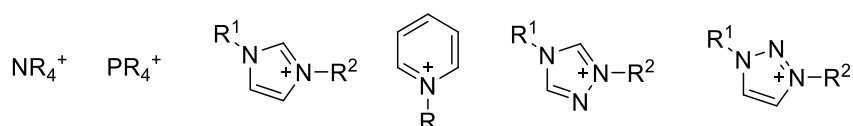


Figure 20: General representation of several cations in ionic liquids. From left to right: ammonium, phosphonium, imidazolium, pyridinium, 1,2,4-triazolium and 1,2,3-triazolium

It is very well documented that the use of a co-catalyst is desirable to help the epoxide ring-opening, i.e. the initial nucleophilic attack.[130-135] One of the employed classes of co-catalysts is represented by Lewis acids since they can favor the formation of a Lewis acid-base adduct, for instance between a Lewis acid and the oxygen of the oxirane which is a Lewis base. Another class of co-catalysts displaying a different activation pathway is represented by the alcohols. The last compounds can form an H-bond with the oxygen of the oxirane hence favoring the ring-opening.[136-139] A less explored way is the activation of the CO₂ by a Lewis acid. It is known that the oxygen atoms of this small molecule display a Lewis base character and can coordinate to Lewis acid sites such as metal centres (e.g. Zn, Ni), leading to a more electrophilic carbon atom. This coordination has been proved on various metal centres and complexes and the resulting enhanced electrophilicity was demonstrated by ¹³C NMR and IR measurements.[140, 141]

It would be desirable to recover easily the catalysts, notably to be consistent with the principles of Green Chemistry, deeply investigated later. The preferred way is the heterogenization of an ionic liquid on a solid support. The cation is covalently linked to the solid surface while the anion is relatively free, only maintained close to the solid by electrostatic interactions with its cation. Indeed, the catalyst is heterogeneous, so easily recoverable and reusable but the anion has a high mobility around the surface. To enhance the catalytic activity, Lewis acids such as ZnBr₂ or ZnCl₂ [142-144] or alcohols [145] to play the role of co-catalyst were also added under homogeneous conditions. In this case, the catalyst is heterogeneous and the co-catalyst is homogeneous.

Another largely employed combination of catalysts and co-catalysts uses a heterogeneous Lewis acid with an ionic liquid (sometimes called additive) in homogeneous phase.[146-148] One of the most known examples is represented by the use of a MOF-based catalysts with Lewis acid properties in the presence of tetrabutylammonium bromide. [149] Other works report the employ of modified graphite as graphite oxide in the presence of different imidazolium halides.[150]

Hereafter, some reports from the literature are briefly presented to give an overview of all the possible heterogenization processes, using various cations, anions, supports, techniques and co-catalysts.

To start, the heterogenization of ammonium-based salts was reported on SiO₂ [151, 152], carbon nanotubes [153] or metal-organic framework (MOF)[154, 155] by covalent functionalization of the surface of the support with the IL. The influence of metal elements in the silica structure as well as the presence of carboxylic acids (as H-bond donor) on the surface

of the nanotubes were also evaluated and the activity of the catalysts was compared to the sole contribution from the ammonium.[151-153] In addition to these issues, a thorough investigation must be done to evaluate the potential applicability of the supports considering e.g. the very elevated cost of production and of carbon nanotubes or the stability of the MOFs. Like ammonium, phosphonium salts were also employed as catalysts on various supports with a similar strategy since the structure is very analogous. A covalent link is generated between the phosphonium-based salt and the support which can be silica,[156-158] alumina [157] or polystyrene.[156, 158] The positive influence of the silica support as well as the presence of alcohol groups was studied.[156-158]

The anchoring of cyclic cations such as imidazolium, pyridinium or triazolium are also presented. Surprisingly, there are very few works related to the use of triazolium salts for the conversion of CO₂. Only one report describes the use of the 1,2,4-triazolium anchored on silica and polystyrene resin using a nucleophilic substitution by 1,2,4-triazole derivative.[159] Zhou et al. reported the generation of a 1,2,3-triazolium through the alkyne-azide click chemistry on a MOF structure (MIL-101-N₃) followed by a quaternization on the N3 position.[160] Maeda et al. reported the same approach in homogeneous phase to functionalise the porphyrin.[125]

An original method for immobilization through non-covalent link was developed by Mirabaud et al. The silica surface was decorated with cavitand acting as host of an ammonium guest. The authors achieved yields comparable to those obtained employing the ammonium salt under homogeneous conditions. This excellent result was attributed to the free movement of both the cation and its anion (halide). Additionally, they anchored the ammonium covalently to the surface and capped the ammonium with the cavitand. Despite the mobility of the halide, they demonstrated a decrease of the catalytic activity compared to the approach using an anchored cavitand while ammonium halide benefit from higher mobility. Both anion and cation are therefore of major importance. [161, 162]

So far, it was reported only the immobilization of one active species on a surface. Interestingly, some authors dedicated special care to the development of an efficient co-catalyst such as porphyrin or salen. Thereafter, they covalently linked it through an ammonium link. This approach has a double role: it allows anchoring a complex molecule which will play the role of co-catalyst and generates an ammonium salt (as catalyst). Several supports were used such as iron oxide nanotubes [163], silica [164-166] or polystyrene [165]. All these supports benefits from very low cost of production or low toxicity.

Co-synthesis strategies were also envisaged by several authors to avoid notably the use of a preformed support. They developed the synthesis of functional monomers that are polymerized

thereafter to generate a solid material.[167-170] The polymerization can occur using a cationic monomer leading to a cationic backbone with free anion around. On the other hand, anionic backbones such as polymethacrylates can be envisaged too with free cations around.[171, 172] Obviously, for the targeted CO₂ conversion with epoxides, it is more desirable to rely on a cationic structure. The halide would have a higher mobility to perform the initial ring-opening of the oxirane. Even if not required, the use of a solid support can be advantageous to guide the polymer and increase its specific surface. This can be performed by polymerization of vinyl-imidazolium around carbon nanotubes [173] or carbon nanohorns.[174] Modified phosphonium salts were polymerized around silica, titania and iron oxide nanoparticles using a plasma technique.[175]

Some authors adapted the use of porphyrin as an efficient co-catalyst to generate a polymer containing both porphyrin and the IL. Wang et al. performed it by mixing a phosphonium and a magnesium porphyrin and the copolymerization occur thanks to the vinyl functions on both of the precursors.[176] Chen et al used a similar strategy by generation in situ of an imidazolium salt through an amine-decorated porphyrin.[177] Jayakumar used a slightly different strategy by mixing imidazolium, pyridinium and porphyrin precursors and 1,4-di(bromomethyl)benzene to polymerise around a carbon nanotube.[178]

A rapid search on the SciFinder search engine with CO₂ and epoxide as key words gave a hit of 11 759 results. Adding ammonium, phosphonium, imidazolium, pyridinium or triazolium as keyword, the engine gave a sharper overview of the results as depicted on the outer circle of the Figure 21. A similar research was performed adding cyclic carbonate as keyword and the repartition of the 1766 hits are represented on the inner circle of the Figure 21. Precising the cyclic carbonate as final product broadened the results of ionic liquids mentioned from 14 % to 29 %. This gives a rapid idea of the efforts dedicated to the application of ammonium salts to the conversion of carbon dioxide. This importance could come from their commercial availability and their direct use in homogeneous phase. The focus was then dedicated to imidazolium.

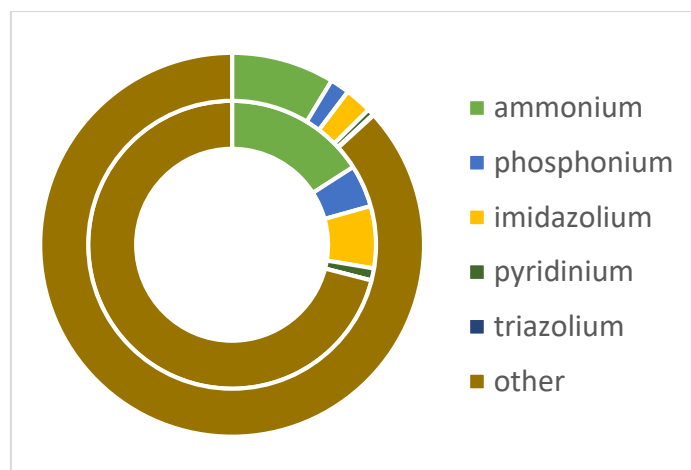


Figure 21: SciFinder hits using keyword CO₂; epoxides (outer circle) and cyclic carbonates (inner circle)

Over the years, there has been a growing interest in the field of the conversion of epoxide and CO₂ to cyclic carbonate. Again, the search engine SciFinder was used and data were sorted by years of publication in Series1 of the Figure 22. A second research was performed adding imidazolium as keyword (Series2).

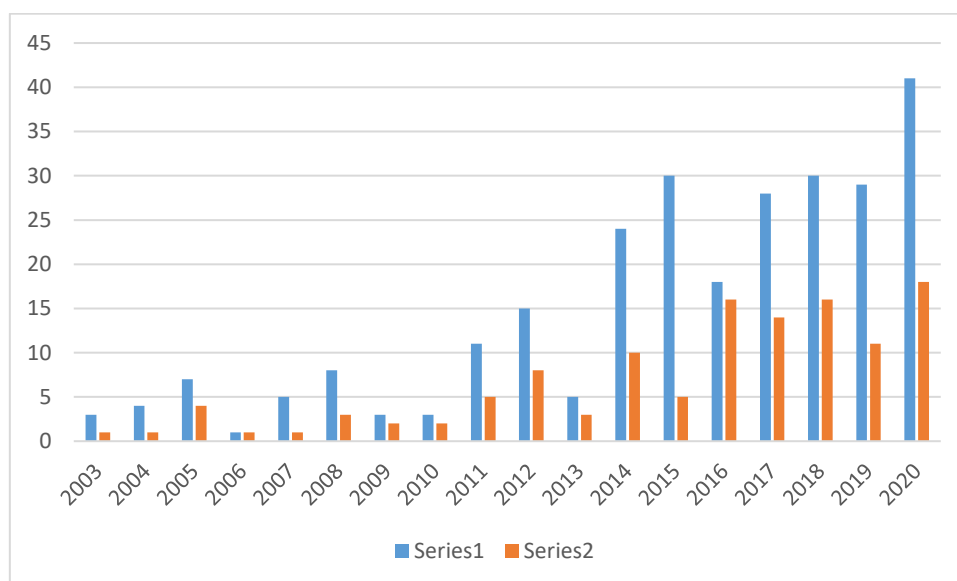


Figure 22: Scifinder hits about epoxide to cyclic carbonate conversion with CO₂ sorted by years of publication (Series1) and including imidazolium (Series2)

Many efforts have been dedicated to the heterogenization of imidazolium salts. Previously mentioned approaches were used such as the direct anchoring on the surface of polymers [179], silica[47, 180], carbon nanostructures[173, 174] or magnetic particles[181]. There is also a growing interest in the synthesis of poly-ionic liquid (PIL) in order to render the imidazolium salt heterogenous without the requirement of a solid support.[182]

Few researches focused on the immobilization of the imidazolium and a Lewis acid on the same support. Latest strategies use various metal-organic framework (MOF) as support and

Lewis acid source. Some authors reported the synthesis of a MOF using a modified terephthalic acid on which imidazolium bromide [183, 184] is anchored by post-functionalization. Other authors used terephthalic acid modified by imidazolium salt as direct organic building unit for the MOF synthesis.[185, 186] Recently, Ding and Jiang proposed an encapsulation of a poly-imidazolium salt inside the MOF porous structure.[187] This is parented to the ship-in-a-bottle strategy. Unfortunately, the stability of MOFs remains a difficulty inherent to the material. Finally, the recyclability of many materials is questionable. Some authors report clearly a lack of reusability. Some other performed those with 100 % conversion, i.e. with an excess of catalyst that does not allow to detect a possible leaching or any decrease in activity.

Green Chemistry

The development of heterogeneous catalysis and the reuse of CO₂ is a perfect example of the application of the principles of Green Chemistry. Green Chemistry is a concept formulated in the 1990's by Anastas and Warner involving 12 principles to perform chemical processes less wasteful and less damaging to the environment.[188]

Nowadays, these concepts tend to be applied more and more. Industrials as well as academics follow the notion detailed thirty years earlier, driven notably by the politics and regulatory agencies that punish the polluters and reward the clean producers.[189] To help a correct assessment of the righteousness, various scale such as the E-factor were established. [190]

In the context of CO₂ utilization and the specific reaction with epoxides to give the corresponding cyclic carbonates, several sustainable principles are respected. A general overview of the reaction is presented hereunder followed by a detailed analysis of the 12 principles of Green Chemistry.

Intrinsically, if a total selectivity is considered, the reaction displays an atom economy of 100 %. Moreover, the reaction can be performed under solvent-free conditions, which avoid additional steps of extraction as well as the use of potentially toxic solvents and the energy and time related. The use of heterogeneous catalysts allows the easy recovering of the catalytically active solid and ideally its reusing in multiple cycles. The variation of pressure is directly proportional to the CO₂ consumption. Some reactors are controlled by mass flow giving a direct measurement of the CO₂ fixation. This is particularly adapted to low pressure reactions, compliantly with security issues mentioned in principle number 12. Particularly, flow chemistry is suitable with this last principle.[164, 165, 191]

An in-depth analysis of all the reagent and principles of the test reaction used in this PhD thesis is given hereafter. The 12 principles are cited and after each principle it is reported how the present research is compliant to those.

1: Prevent Waste

It is better to prevent waste than to treat or clean after it has been created

- A renewable source of carbon is used, no toxic by-products are generated
- Selectivity is often total
- The catalyst (if heterogenous) can be easily recovered and reused

2: Atom Economy

Synthetic methods should be designed to maximize incorporation of all starting materials into the final product

- The atom economy of the reaction is 100 %.

3: Less Hazardous Synthesis

Use and generate substances that possess little or no toxicity to human health and environment

- Carbon dioxide is a non-toxic and non-flammable gas.
- Most of the epoxides are carcinogenic and/or can cause damages the central nervous system.
- Ethylene oxide presents risks of explosion
- But there is a net increase in safety compared to the previous reported phosgene-based method

4: Design Benign Chemicals

Chemical products should be designed to preserve efficacy of function while reducing toxicity

- Carbonates are not particularly toxic

5: Benign Solvents and Auxiliaries

The use of auxiliary substances (solvents, separation agents) should be made unnecessary/innocuous

- The reaction is performed under solvent-free conditions
- The selectivity to the desired product is often complete The recovery of the solid catalyst is performed via simple centrifugation or filtration

6: Design for Energy Efficiency

Energy requirements should be minimized. Synthetic methods should be conducted at ambient temperature and pressure

- Part of the thesis goal is to improve the activation step to reduce the reaction temperature
- Studies demonstrated that the influence of the pressure is not crucial and synthesis can be performed at relatively low pressure (< 10 bar)

7: Use of renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting

- CO₂ is a renewable feedstock

8: Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/deprotection) should be minimized/avoided. Such steps require additional reagents and can generate waste

- The reaction is straightforward
- The catalyst can be recovered and reused

9: Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents

10: Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment

- Most of the carbonates are not persistent in nature

11: Real-Time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances

- The reactor used for catalytic tests is equipped with an electronic pressure gauge. It enables a real-time monitoring of the reaction

12: Inherently Benign Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents

- The possibility to work at relatively low pressure and the research for low temperature synthesis limit the possibility of explosion due to the pressure

Considering the high potential for functionalization and therefor as catalyst of mesoporous silica materials and the interest of using CO₂ as feedstock for the production of cyclic carbonates, it is proposed to focus on the heterogenization of imidazolium salts together with a co-catalyst component. This is detailed in the following Thesis outlines.

Thesis outlines

The importance of CO₂ as feedstock in the field of Green Chemistry and the particular interest of the coupling of CO₂ with epoxide to form cyclic carbonates was demonstrated previously. It is highly desirable to develop easily recoverable and reusable catalysts to achieve this goal and to stay even closer to the principles of sustainable chemistry. In this context, the design of highly efficient (both in terms of conversion and selectivity) heterogeneous catalysts play a decisive role. Over the years, the development of heterogeneous catalysts was enhanced through the development of (meso)porous silica networks that present a large window of possible morphology, size and porosity. More importantly, silica-based solids display a broad potential of functionalization via co-synthesis or post-functionalization strategies. These strategies can be employed for the functionalization of the silica support with organic moieties, inorganic nanoparticles or single-site substitution.

Among the literature, there are multiple examples of heterogenization either of the catalyst or of the co-catalyst. Only few authors report fully heterogeneous catalysts embedding both Lewis acid as co-catalyst and the imidazolium salt as main catalyst. Even fewer are reusable over multiple cycles. Here, it is chosen to use mesoporous silica network and its wide possibilities to be functionalized to develop new catalysts using both co- and post-functionalization of the silica. They are also particularly suitable thanks to their stability.

In the first chapter, the general strategy employed is set up. A mesoporous silica network embedding Sn or Zn as single-site in the SiO₂ architecture was realised using a co-synthesis approach. The presence of these metal cations as single site generates a Lewis acidity, i.e. the co-catalyst. Then, the imidazolium salt, i.e. the main catalyst was anchored on the surface via a one-pot reaction using at the same time N-methylimidazole and 3-chloropropyltrimethoxysilane to generate and anchor simultaneously the imidazolium chloride. After synthesis, the materials were fully characterized. A special attention was dedicated to the acidity of the solids and to the possible synergic role of Lewis acid and imidazolium salts on the catalytic performances of the bi-functional catalysts. The influence of the Sn and Zn to enhance the catalytic activity was investigated and the results were compared with the corresponding metal-free material.

Along the different chapters, the designed material was modified to improve its catalytic performances by varying the metal inserted (Sn, Zn, Ti, Al) or the imidazolium moieties anchored. The objective was to understand activation ability of the co-catalyst while improving the catalysts performances.

In the second chapter, the nature of the anchored imidazolium salt was modified. The initial aim was to add alcohol moieties able to create H-bond with the epoxide and to verify if the Lewis acid moiety (represented by the Sn centres) could be able to directly activate the CO₂. Experiments of CO₂ adsorption coupled with IR experiment demonstrated the principle that the CO₂, usually neglected in the literature, is also activated by the material. This result push forward the understanding of the reaction mechanism.

The isomorphic substitution of silicon with Ti was performed in the third chapter. In this case, the importance of the presence of Ti as single site was dual. On the one hand, it plays a fundamental role (as Lewis acid centre) to enhance the activity of the solid in the synthesis of cyclic carbonates. On the other hands the titanium-based solid revealed an efficient catalyst for the epoxidation reaction. This would lead to a cascade reaction from alkenes to epoxide to cyclic carbonate.

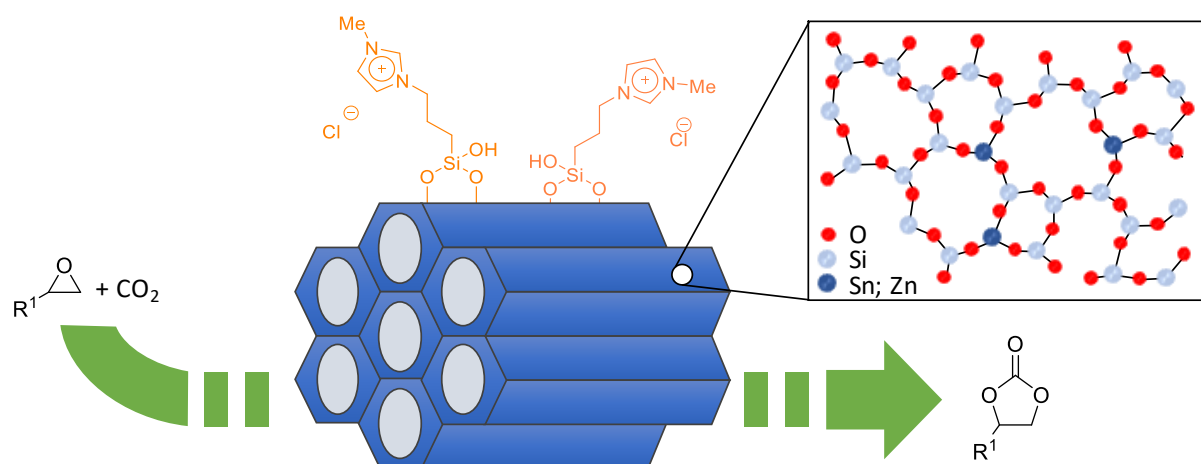
It seems almost impossible to bypass the use of aluminosilicates when discussing about acidic materials. For this reason, in the 4th chapter the use of aluminosilicates with SBA-15 structure was envisaged. To extend the understanding of the co-activation mechanism, the solids were functionalized with MgO or imidazolium chloride. The idea was to verify the synergetic effect of Al centre with MgO compared to the synergetic effect of the unrestrained chloride from imidazolium salt.

In the final chapter, a novel approach with organoboron was developed. The control of the acidity was met via the various substitution around the boron atom. This represents a library toward the tuning to the most suitable Lewis acidity. It is desirable to have a good activation of the epoxide but a too strong interaction blocking the intermediate must be avoided. The successful anchoring of the newly developed borane on silica surface as well as imidazolium salt opens the door to a wide field of possibility.

In the whole thesis, various characterization techniques were employed to verify all the steps of synthesis as well as the interaction of the materials with the reactant. A particular attention is dedicated to the comprehension of the activation mechanism of the reactants by the co-activator. The main interest of the heterogeneous catalysis is the reusability of the catalyst. Recyclability procedure and tests were set up to ensure this reusability. The robustness of the material was then assessed in every steps of the present work.

Chapter I

Bi-functional heterogeneous catalysts for carbon dioxide conversion: enhanced performances at low temperature



Abstract

Novel heterogeneous bi-functional catalysts bearing tin or zinc inserted as single sites within the silica architecture acting as acid centres and decorated with imidazolium moieties as nucleophile source were successfully synthesized. The materials were extensively characterized via various techniques including N₂ physisorption, solid state nuclear magnetic resonance, X-ray photoelectron spectroscopy, transmission electron microscopy and adsorption microcalorimetry. The solids were tested as catalysts for the conversion of carbon dioxide, selecting the synthesis of styrene carbonate as target reaction. Both materials exhibited improved performances compared to the analogous solids functionalized with the sole imidazolium salt as well as to other materials reported in the literature. The Sn-based catalyst displayed excellent conversion also in presence of various epoxides. In all experiments the bi-functional solid allowed reducing the reaction temperature below 150 °C. In presence of glycidol the temperature was decreased down to 30 °C. The short synthesis protocol of the heterogeneous catalysts, together with the 100 % atom economy of the target reaction and the low reaction temperature, make the entire process highly sustainable. Moreover, the Sn-based catalyst resulted stable under the selected reaction conditions and reusable in multiple catalytic cycles

The results presented in this chapter have been published in:

A. Comès, X. Collard, L. Fusaro, L. Atzori, M.G. Cutrufello, C. Aprile, Bi-functional heterogeneous catalysts for carbon dioxide conversion: enhanced performances at low temperature, RSC Advances, 8 (2018) 25342-25350.

Introduction

In this first chapter, the design of two novel bi-functional heterogeneous catalysts is presented. These solids display both a metal centre (Zn or Sn) able to bring acid properties and the nucleophile required to promote the opening of the epoxide. The synthesis procedure involved the initial preparation of a porous support bearing the metal element inserted as single sites within the silica architecture followed by the grafting of an imidazolium salt. The solids were extensively characterized via various techniques including N₂ physisorption, X-ray diffraction, ¹³C and ²⁹Si solid state nuclear magnetic resonance, transmission electron microscopy, combustion chemical analysis and inductively coupled plasma optical emission spectroscopy. The insertion of Sn and Zn as single sites within the silica structure was proved via solid state ¹¹⁹Sn nuclear magnetic resonance and X-ray photoelectron spectroscopy respectively, while the acid properties of the solids were addressed via adsorption microcalorimetry.

The materials were tested under solvent-free conditions in a batch reactor selecting the chemical fixation of CO₂ into styrene oxide as target reaction. Both Sn- and Zn-based solids displayed improved performances compared to the analogous silica catalyst functionalized with the sole imidazolium salt as well as to other solids reported in the literature. The versatility of the Sn-based catalyst was also tested with a series of epoxides. In all experiments, the bi-functional solid allowed decreasing the reaction temperature below 150 °C.

Results and discussion

The design of the bi-functional heterogeneous solids bearing both imidazolium-based catalysts and co-catalysts with acid properties was based on a two-step procedure.

In a first step, mesoporous solid supports bearing Sn and Zn embedded as single site in the silica structure were successfully synthesized optimizing a previously described procedure.[16, 17] The selected approach allows obtaining particles with reduced size (below 100 nm) with a short protocol requiring only 60 min synthesis time, at ambient temperature, using highly diluted NH₃ as base to catalyse the hydrolysis-condensation reaction. These particular synthesis condition allowed to produce extra-small mesoporous silica particles. This range of size was initially selected because of the improved performances of the catalysts displaying a small particle dimension compared to the large particle analogues.[18] For the sake of comparison, a mesoporous all-silica solid (SiO₂) with reduced size was synthesized as well. Transmission electron microscopy investigation confirmed that both Sn- and Zn-based solids (Sn-SiO₂ and

Zn-SiO₂) as well as metal-free silica display a narrow particle size distribution with a particle diameter comprised between 50 and 100 nm (Figure 1).

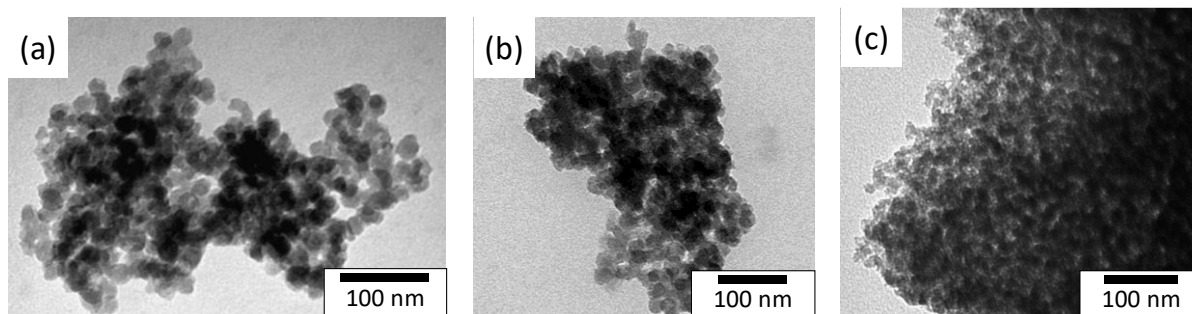


Figure 1: TEM images of SiO₂ (a), Sn-SiO₂ (b) and Zn-SiO₂ (c)

The characteristic hexagonal organization of pores was confirmed via low-angle XRD measurements (Figure S1). All samples display the d_{100} signal at $2\theta \cong 2^\circ$, typical of MCM-41-like architectures. As expected, the main d_{100} reflection was broader than the one observed for MCM-41 with standard dimensions and the additional d_{110} and d_{200} reflections were not clearly visible as a consequence of the reduced size with a consequent decrease of the long range order.[19] Analysis of the materials via nitrogen physisorption revealed a high specific surface area and a narrow pore size distribution centred at 2.2 nm (Table 1 and Figures 6 and S2).

In view of the selected application, a key parameter is represented by the acidity of the solids, which was investigated by means of adsorption microcalorimetry. In Figure 2, the differential heat of adsorption, Q_{diff} , is reported as a function of the amount of NH₃ adsorbed for both Sn-SiO₂ and Zn-SiO₂ samples. For comparison, the analysis of SiO₂ is reported as well. From this investigation emerged that the thermal effect associated with ammonia adsorption on Sn-SiO₂ and Zn-SiO₂ is much higher than on metal-free SiO₂, especially at low NH₃ uptake values, indicating that both Sn- and Zn-based solids display acid properties significantly more pronounced than the all-silica sample. On both Sn-SiO₂ and Zn-SiO₂, Q_{diff} is initially higher than 200 kJ/mol, revealing the presence of strong acid sites, and then decreases as the ammonia uptake increases. The point at which the adsorption becomes non-specific can be established taking into account the results obtained on the pure silica sample, for which differential adsorption heat values as high as 67 kJ/mol are observed (Figure 2), in agreement with previous experiments on pure silica samples.[192-194] Accordingly, for the Sn- and Zn-based samples the fraction of ammonia uptake corresponding to differential heats below 70 kJ/mol was ascribed to non-specific and/or physical adsorption on the pure-silica part of the samples, and thus neglected in calculating the acid sites concentration which resulted 170 and 280 $\mu\text{mol/g}$ for Sn-SiO₂ and Zn-SiO₂, respectively.

Table 1: Textural properties of the solids

	Specific Surface Area (m ² /g)	Mean Size (nm)	Pore Volume (cm ³ /g)	Pore Amount Imi (mmol/g) ^[a]	of Amount of M (mmol/g) ^[b]
SiO ₂	1090	2.1	1.24	/	/
SiO ₂ -imi	239	0.8	0.58	1.46	/
Sn-SiO ₂	1086	2.3	1.43	/	not measured
Sn-SiO ₂ -imi	234	0.8	0.71	1.25-1.40	0.16
Zn-SiO ₂	1125	2.2	1.37	/	not measured
Zn-SiO ₂ -imi	298	0.8	0.60	1.30 - 1.37	0.10

^[a] Range of imidazolium salt determined via combustion chemical analysis on different batches. Amount estimated considering the nitrogen percentage.

^[b] Amount of metal (M: Sn or Zn) determined via inductively coupled plasma optical emission spectroscopy (ICP-OES). See experimental section for more details

The continuous decrease in the differential heat as the ammonia uptake increases on both samples indicates heterogeneity of the acid sites, which can be either Lewis (the Sn or Zn centres) or Brønsted sites (bridged OH groups made acidic by the proximity of the metal site). From the data of ammonia readsorption after overnight evacuation, it was possible to evaluate the differential heat at which the adsorption shifts from irreversible to reversible. It was found that the acid sites able to adsorb ammonia irreversibly are those characterized by Q_{diff} values higher than 90 kJ/mol, whose concentration is about 110 and 160 $\mu\text{mol/g}$ for Sn-SiO₂ and Zn-SiO₂, respectively. From this study emerged that both materials display interesting acid properties in view of their possible application as active supports in the conversion of carbon dioxide.

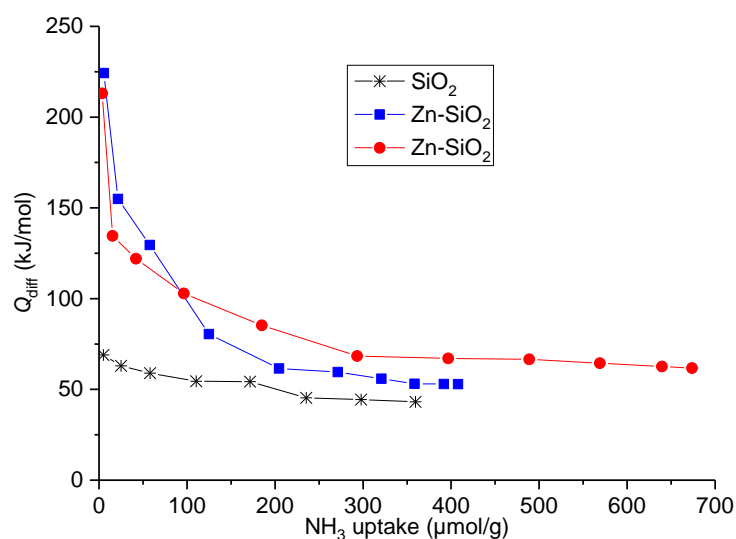
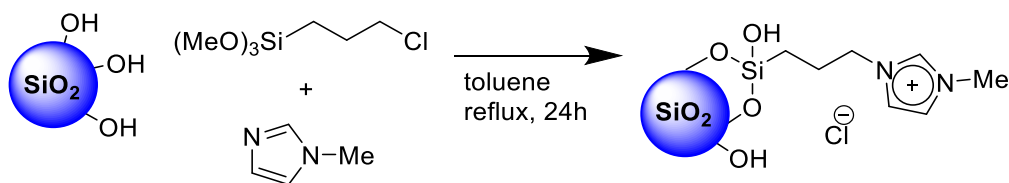


Figure 2: Differential heat of adsorption (Q_{diff}) as a function of the NH_3 uptake for $Sn-SiO_2$; $Zn-SiO_2$ and SiO_2

The second step, requiring the functionalization of the surface with an imidazolium-based catalyst, was performed via a one-pot procedure reacting the previously described solids with an equivalent mixture of 3-chloropropyltrimethoxysilane and 1-methyl imidazole as depicted on Scheme 1. This procedure, compared with the standard two-step approach, presents the multiple advantages of a fast functionalization together with a limited number of separation and purification procedures as well as the absence of intermediate characterizations. The amount of organic moieties in the functionalized solids (SiO_2 -imi; $Sn-SiO_2$ -imi and $Zn-SiO_2$ -imi) was quantified via combustion chemical analysis (Table 1) while the proof of the presence of imidazolium and not adsorbed imidazole species was obtained via solid state ^{13}C -CP-MAS NMR (Figure 3).[195, 196] The anchoring of the trimethoxysilane-based linker to the silica surface was addressed via solid state ^{29}Si NMR performed in cross polarisation.



Scheme 1: One-pot functionalization of silica materials with imidazolium salt

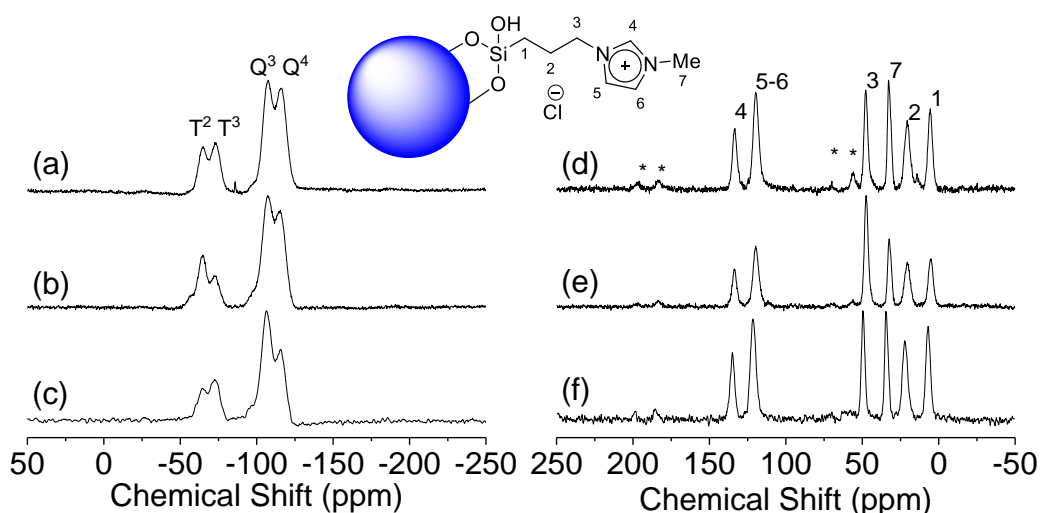


Figure 3: ²⁹Si and ¹³C-CP-MAS-NMR of SiO₂-imi (a; d), Sn-SiO₂-imi (b; e) and Zn-SiO₂-imi (c; f)

The presence of a combination of T³ and T² signals in the ²⁹Si-CP-MAS-NMR (Figure 3) confirmed that organic moieties were anchored via a covalent bond and not physisorbed on the silica surface.

A deep investigation on the insertion of Sn and Zn as single site within the silica scaffold was performed as well. Solid-state ¹¹⁹Sn-NMR under static conditions (Figure 4, left) revealed the presence a broad band centred at -680 ppm which can be attributed to Sn(IV) species in a tetrahedral coordination.[197-199] The absence of relevant contribution at higher frequencies (around -600 ppm) allows excluding the formation of a significant amount of SnO₂ due to self-condensation of the tin precursors in the reaction medium. The acquisition of solid ⁶⁷Zn NMR data was hindered by the intrinsic difficulties of this nucleus. It is known that the low natural abundance of ⁶⁷Zn together with its large quadrupole moment and the small gyromagnetic ratio represent a highly unfavourable combination of features for solid state nuclear magnetic resonance investigation.[200] Moreover, the low amount of Zn inserted in the samples (about 2 wt%) reduces also the possibility of efficient use of advanced sensitivity-enhancement techniques or ultrahigh-magnetic-field NMR instruments for a deep investigation of the Zn coordination sphere. In order to overcome these drawbacks, X-ray photoelectron spectroscopy via analysis of the Auger transition (Figure 4, right) was used to study the insertion of Zn as single site in the MCM-41 solid. The Zn LMM Auger transition can be considered as an overlapping of two different contributions, the first one centred at 988.08 eV corresponds to extra-framework ZnO and the second one at 985.30 eV can be attributed to intra-framework Zn species.[17] This result indicates that in the case of Zn-SiO₂-imi the metal centre is partially present (*ca.* 30 % of the total amount) in the form of ZnO extra-framework species.

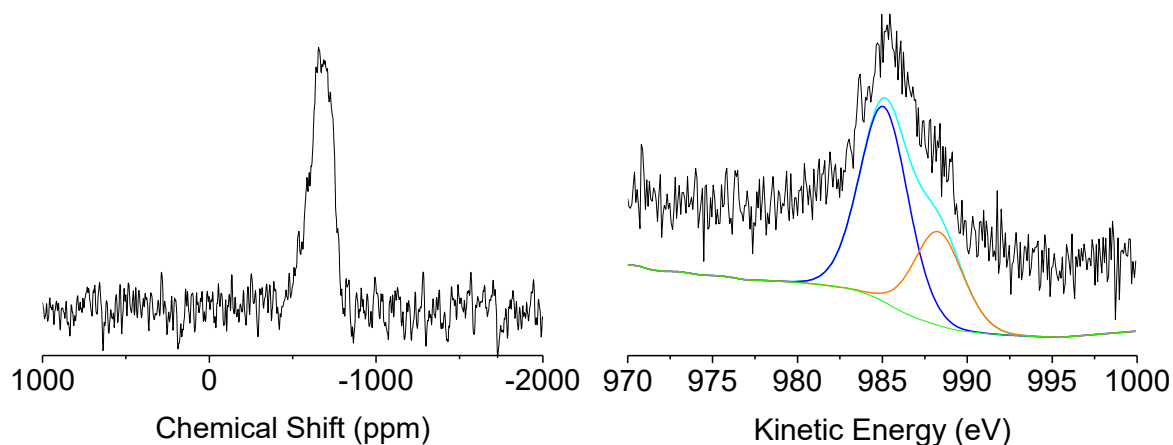


Figure 4: Solid-state ^{119}Sn NMR of Sn-SiO_2 (left) and Zn LMM Auger transition of Zn-SiO_2 (right)

The structural and textural properties of the final materials ($\text{Sn-SiO}_2\text{-imi}$ and $\text{Zn-SiO}_2\text{-imi}$) were investigated via transmission electron microscopy (TEM), X-ray diffraction (XRD) and nitrogen physisorption. TEM analysis of the samples (Figure 5) revealed that the post-functionalization did not affect the morphology of the materials with aggregation or sintering phenomena. Both $\text{Sn-SiO}_2\text{-imi}$ and $\text{Zn-SiO}_2\text{-imi}$ display an almost spherical shape and a narrow particle size distribution similar to the non-functionalized samples. As expected, low angle XRD measurements performed on the imidazolium functionalized solids evidenced a pattern similar to the one already observed for Sn-SiO_2 and Zn-SiO_2 (Figure S1) confirming that the hexagonal order was preserved during the reaction. As expected, nitrogen physisorption analysis (Figure 6) clearly indicated a decrease of the Brunauer-Emmet-Teller (BET) specific surface area as well as of the pore diameter (psd). Due to the shift of the pore size distribution in the microporous region two different methods were applied for the analysis of the data. The standard Barrett-Joyner-Halenda (BJH) was selected to estimate the psd of the non-functionalized solids while the micropore size was evaluated using the method proposed by Horwath and Kawazoe (Figure S2).[201, 202]

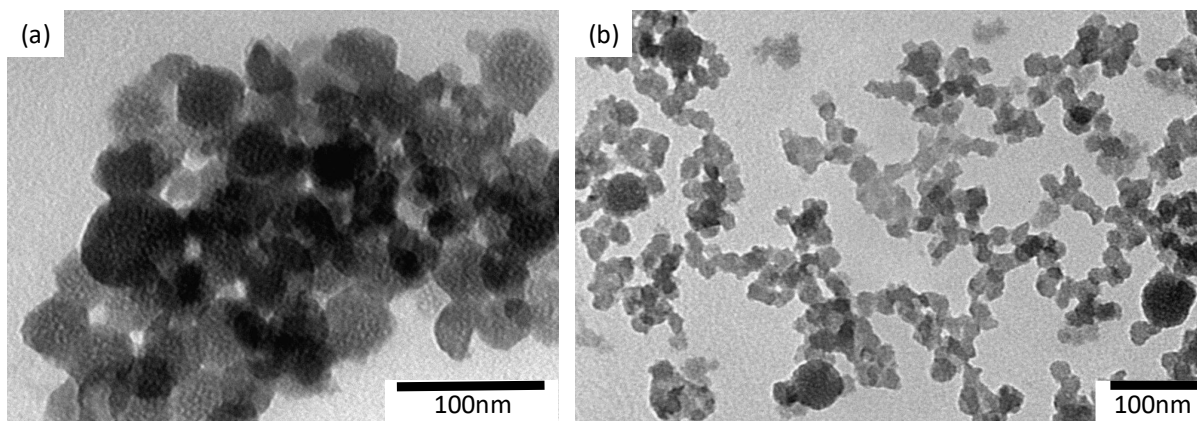


Figure 5: TEM images of Sn-SiO₂-imi (a) and Zn-SiO₂-imi (b)

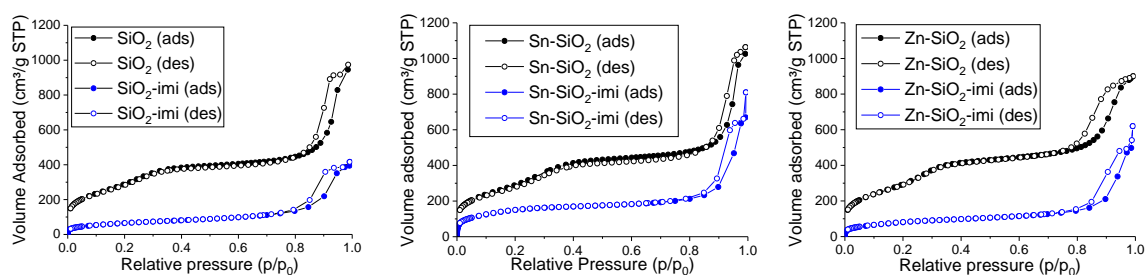


Figure 6: N₂ adsorption-desorption isotherm of SiO₂; Sn-SiO₂ and Zn-SiO₂ and their corresponding imidazolium-functionalized homologues.

The variation of the pore diameter suggests that the anchoring of the imidazolium moieties occurs not only at the external surface of the particles but also within the pores. It is important to underline that the reduced pore size does not represent a serious drawback in view of the application of these solids in the conversion of carbon dioxide because of the small size of the reactants. As can be seen in Figure 6 all the materials display a type IV isotherm with an evident hysteresis loop at high relative pressures. This behaviour was previously observed for the materials exhibiting an extra-small size [16, 18] and can be ascribed to the presence of disordered meso-macro pores as a consequence of the inter-particle interactions. A condensation between particles can even be claimed considering the high temperature treatment performed to remove the surfactant leading to this unordered porosity. Both Sn-SiO₂-imi and Zn-SiO₂-imi display promising properties for catalytic applications such as high surface area, relevant amount of metal element inserted as single site which provide the desired acidity and good percentage of imidazolium functionalization. Hence, both solids were tested in the reaction of carbon dioxide with epoxides to give the corresponding cyclic carbonates. A challenging substrate as styrene oxide was selected to evaluate the activity of the catalysts and the reaction temperature was decreased to 125 °C compared to the standard value (usually this reaction is performed at 150 °C in absence of co-catalyst).[173, 203] For comparison, the

activity of the all-silica MCM-41 solid functionalized with imidazolium moiety ($\text{SiO}_2\text{-imi}$) was studied as well (see entry 1 in Table 2). Moreover, before starting the investigation in the presence of the bi-functional catalysts an additional catalytic test adding a small amount of ZnCl_2 (corresponding approximatively to the quantity inserted in the silica framework) to the reaction mixture was performed in order to evaluate the positive contribution of a salt with Lewis acid properties under homogeneous conditions. In order to allow a meaningful comparison among the solids, as well as with reference catalysts reported in the literature, two different turnover numbers (TON) were calculated. This choice is justified by the presence of two different catalytic active species behaving as catalyst (imidazolium moieties) and co-catalysts (metal inserted as single site) both displaying a synergic role in the reaction. The TON considering the catalyst (TON_{imi}) was defined as moles of epoxide converted/moles of imidazolium salt while the TON based on the co-catalyst (TON_{M}) was defined as moles of epoxide converted/moles of Sn or Zn.

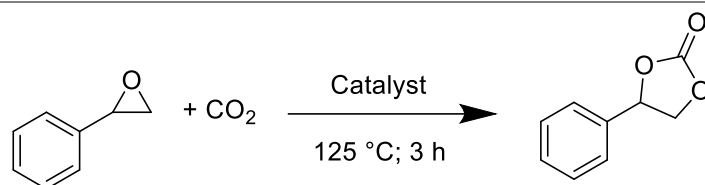
As expected, the presence of ZnCl_2 caused an improvement of the catalytic performances of the $\text{SiO}_2\text{-imi}$ solid from 54 % to 63 % conversion (compare entries 1 and 2 in table 2). Interestingly in the presence of Sn- $\text{SiO}_2\text{-imi}$ similar performances compared to the homogeneous Lewis acid catalyst were obtained. The activity of the Sn- $\text{SiO}_2\text{-imi}$ solid was preserved after decreasing the amount of catalyst (table 2, entries 3 and 4). The slightly increase of TON_{imi} obtained under the conditions reported in entry 4 could be attributed to a better dispersion of the solid in the reaction mixture. Zn- $\text{SiO}_2\text{-imi}$ catalyst allowed achieving similar conversion (compare entries 4 and 5 in table 2), thus further proving the positive influence of the insertion of single sites within the silica structure.

All the previously described experiments were performed under the same reaction conditions, hence in presence of a small amount (1.5 mL) of ethanol needed to solubilize the ZnCl_2 added in the initial test. However, since it is known that the presence of hydroxyl groups in the reaction mixture may also facilitate the opening of the epoxide via formation of hydrogen bonds, analogous experiments in the absence of alcohol were performed as well.

No relevant differences were observed for both Sn- $\text{SiO}_2\text{-imi}$ and Zn- $\text{SiO}_2\text{-imi}$ catalysts (compare entries 4 with 6 and 5 with 7), thus proving that the small amount of ethanol was not the main responsible of the increased activity and further confirming the positive active role of the Sn- SiO_2 and Zn- SiO_2 supports.

The better performances of Zn- $\text{SiO}_2\text{-imi}$ in terms of TON_{M} could be attributed to the higher acidity of the support.

Table 2: Conversion of styrene oxide into the corresponding cyclic carbonate with use of different catalysts



Entry	Catalyst	Amount (g)	EtOH (mL)	Conversion (%)	Selectivity (%)	TON _{imi} ^[a]	TON _M ^[b]
1	SiO ₂ -imi	1	1.5	54	>95	78	-
2	SiO ₂ -imi ^[c]	1	1.5	63	>95	91	901
3	Sn-SiO ₂ -imi	1	1.5	60	>95	94	774
4	Sn-SiO ₂ -imi	0.5	1.5	37	>95	116	948
5	Zn-SiO ₂ -imi	0.5	1.5	39	>95	127	1489
6	Sn-SiO ₂ -imi	0.5	-	32	>95	96	826
7	Zn-SiO ₂ -imi	0.5	-	32	>95	98	1343

Reaction conditions: styrene oxide (24.0 mL; 210 mmol), CO₂ pressure (40 bar), temperature (125 °C), 500 rpm, 3 h

^[a] Turnover number (TON) calculated as moles of epoxide converted/moles of imidazolium sites. Amount of imidazolium salt quantified via combustion chemical analysis for each catalyst

^[b] Turnover number (TON) calculated as moles of epoxide converted/moles of Sn or Zn. Amount of metal (Sn or Zn) quantified via inductively coupled plasma optical emission spectroscopy (ICP-OES) for each catalyst

^[c] Reaction performed in presence of ZnCl₂ (20 mg, 0.147 mmol)

The versatility of the catalysts was checked selecting the most challenging (slightly less performant) Sn-SiO₂-imi solid. The data concerning the activity of the Sn-based material in the presence of various epoxides are reported in Table 3. From this investigation emerged that the Sn-SiO₂-imi displays excellent performances in the presence of various epoxides including the extremely low reactive cyclohexene oxide (Entries 1-2). Moreover, in the presence of epichlorohydrin and glycidol excellent performances were achieved at the challenging temperatures of 80 °C and 60 °C respectively (Entries 7 and 9). All these results confirm the positive synergic effect of the catalyst and co-catalyst as well as the great influence of the working temperature.

Table 3: Conversion of various epoxides into corresponding cyclic carbonates with use of Sn-SiO₂-imi as catalyst

Entry	Substrate	Temperature (°C)	Conversion (%)	Selectivity (%)	TON _{imi} ^[a]
1 ^[b]	Cyclohexene oxide	150	26	>95	90
2 ^[b]	Cyclohexene oxide	125	5	>95	17
3	Styrene oxide	125	32	>95	96
4	Propylene oxide	125	41	>95	196
5	Epichlorhydrin	125	53	>95	233
6	Epichlorhydrin	100	40	>95	185
7	Epichlorhydrin	80	16	>95	78
8	Glycidol	80	63	>95	334
9	Glycidol	60	35	>95	179
10 ^[c]	Glycidol	30	11	>95	32

Reaction conditions: epoxide (24.0 mL), catalyst (500 mg), CO₂ pressure (40 bar), 500 rpm, 3 h

^[a] Turnover number (TON_{imi}) calculated as moles of epoxides converted/moles of imidazolium active sites. Amount of imidazolium salts quantified via combustion chemical analysis for each catalyst (not all the catalyst used comes from the same preparation)

^[b] Reaction performed for 24 h

^[c] Reaction performed for 6 h with 1 g of catalyst

To challenge even more the Sn-SiO₂-imi, a test with glycidol at 30 °C (entry 10) was performed as well. Also under these conditions, the catalyst showed a good TON_{imi}, higher than other bi-functional catalysts reported in the literature employed under homogeneous^[130] (TON_{imi} of 26) or heterogeneous conditions in the presence of the same epoxide.

In the recent literature, many efforts were dedicated to the decrease of the working temperature and/or pressure (e.g. using MOF). However, this goal is usually achieved employing imidazolium or more often ammonium salts in homogeneous phase.^[146, 204-208] It should be mentioned that a direct comparison with the literature is hampered by the huge differences in the reaction conditions employed for the synthesis of cyclic carbonates including presence

of solvent, substrate to catalyst molar ratio, nature of nucleophile, use of co-catalyst, temperature, pressure and reaction time. These difficulties can be partially reduced if the catalysts are compared in terms of turnover number or turnover frequency (TOF defined as TON/time). Our solids display better TON_{imi} than some of the most active catalysts previously reported in the literature and used in the absence of co-catalyst. Moreover, they also display excellent TON_{M} or TOF_{M} if compared with other bi-functional heterogeneous catalysts. One of the best comparison can be probably done with similar silica-based porous materials embedding titanium as single site[209] and tested in the presence of styrene oxide at 120 °C under solvent free conditions displayed TON_{M} much lower than the ones achieved with both Sn-SiO₂-imi and Zn-SiO₂-imi. Other metal-free catalysts containing only imidazolium-based species can be also selected for comparison to evidence the importance of the co-catalysts. One of the most active silica-supported imidazolium salts displayed a TON_{Imi} of 88 in presence of styrene oxide and under conditions similar to those used for the present work. However, it deserve to be mentioned that the counter-anion/nucleophile used was the more active iodide.[47]

Still considering the synthesis of styrene carbonate, similar TON (e.g. 101 and 106) were achieved with other structured supports such as carbon nanohorns but these catalysts required higher temperature (150 °C).[174]

When working under heterogeneous conditions, the excellent catalytic performances of a solid are not the only parameter to be considered, the true heterogeneous nature of the catalyst should be also evaluated. In order to exclude the possible leaching of active species in solution and confirm the stability of catalyst under the selected reactions conditions, recycle experiments were performed (Figure 7). After each cycle, the Sn-SiO₂-imi catalyst was recovered from the reaction mixture by centrifugation, washed and reused (see experimental section for more details) without any additional activation treatment. The data reported in Figure 7 evidence that the catalyst can be used in multiple cycles without any decrease in the catalytic performances.

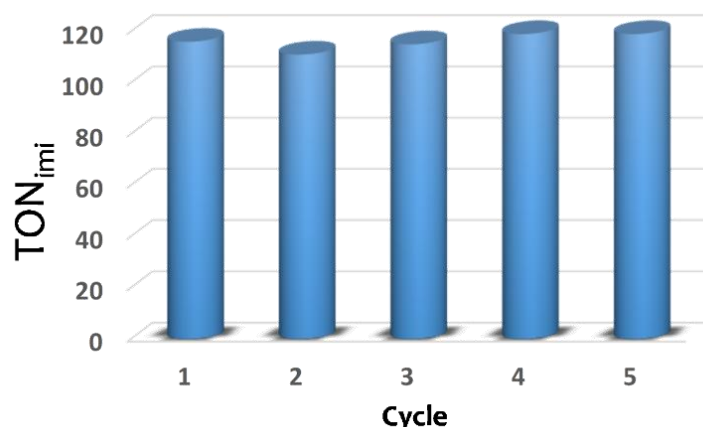


Figure 7: Catalytic performance of Sn-SiO₂-imi in subsequent reaction cycles

Conclusions

Two bi-functional silica-based materials bearing tin or zinc inserted as single sites within the silica architecture acting as acid centres and decorated with imidazolium moieties as nucleophile source (Sn-SiO₂-imi and Zn-SiO₂-imi) were successfully synthesized. The solids display promising features for catalytic applications including high surface area, reduced particle size, good amount of imidazolium salts and acid properties estimated via microcalorimetry analysis. Both Sn-SiO₂-imi and Zn-SiO₂-imi were used as catalyst for the chemical fixation of carbon dioxide onto epoxides to give the corresponding cyclic carbonates, displaying excellent performances. The versatility of the Sn-based catalyst was proved in the presence of various epoxides. In all experiments, the bi-functional solids allow reducing the reaction temperature below 150 °C. Moreover, with glycidol the temperature was decreased down to 30 °C. The short synthesis protocol of the heterogeneous catalysts, together with the 100 % atom economy of the target reaction and the low reaction temperature make the entire process highly sustainable. Sn-SiO₂-imi catalyst resulted stable under the selected reaction conditions and reusable in multiple catalytic cycles. All these features stand as a basement for future improvement and development of new fully heterogeneous catalysts in the next chapter.

Experimental section

Materials and methods

Ammonium hydroxide (30 %) was purchased from Carl Roth. Cetylmethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), N-methylimidazole, (3-chloropropyl)trimethoxysilane, styrene oxide, epichlorohydrin, cyclohexene oxide, propylene oxide were purchased from TCI. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, glycidol were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

A Tian-Calvet heat flow calorimeter (Setaram) equipped with a volumetric vacuum line was used for microcalorimetric measurements. Each sample was pre-treated overnight at 250 °C under vacuum (10^{-3} Pa). Ammonia adsorption was carried out at 80 °C by admitting successive doses of the probe gas and recording the corresponding thermal effect. The run was stopped at a final pressure of 133.3 Pa. After overnight outgassing at 80 °C, a second adsorption run was carried out.

General procedure for the synthesis of SiO_2 ; Sn-SiO_2 and Zn-SiO_2 solids.

Silica based materials were prepared according a dilute route.[17] Ammonium hydroxide (1.42 mL, 10.95 mmol) and CTAB (1.52 g, 4.16 mmol) were added to 726 mL of milli-Q water. After 30 minutes under agitation, TEOS (6.936 g, 33.29 mmol) and the proper amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (157.6 mg, 0.45 mmol) or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (133.9 mg, 0.450 mmol) previously dissolved in 2 mL of absolute ethanol were added dropwise in the aqueous solution. After 1 h under agitation at room temperature, the solid was filtered and washed 3 times alternatively with water and ethanol. The solid was dried overnight and calcined under air for 8 h at 550 °C with heating and cooling rate of 2 °C/min.

Synthesis of SiO_2 -imi; Sn-SiO_2 -imi and Zn-SiO_2 -imi

The SiO_2 ; Sn-SiO_2 or Zn-SiO_2 solids were dried in oven at 100 °C overnight before functionalization. In a round bottom flask, the solid (1.5 g) was suspended in 15 mL of dry toluene. N-methylimidazole (24 mmol) and (3-chloropropyl)trimethoxysilane (12 mmol) were added. The mixture was stirred at reflux temperature for 24 h. After cooling, the functionalised solid was washed with Soxhlet extractor using methanol as solvent. The amount of imidazolium was evaluated through combustion chemical analysis.

Supporting Information

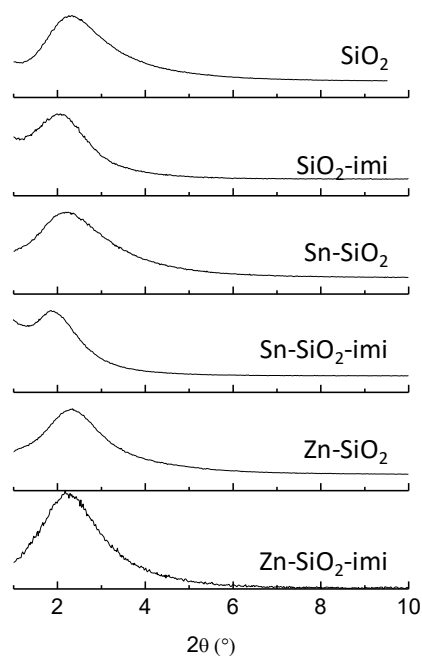


Figure S1: Small angle XRD pattern of SiO_2 ; $\text{SiO}_2\text{-imi}$; Sn-SiO_2 ; $\text{Sn-SiO}_2\text{-imi}$; Zn-SiO_2 and $\text{Zn-SiO}_2\text{-imi}$

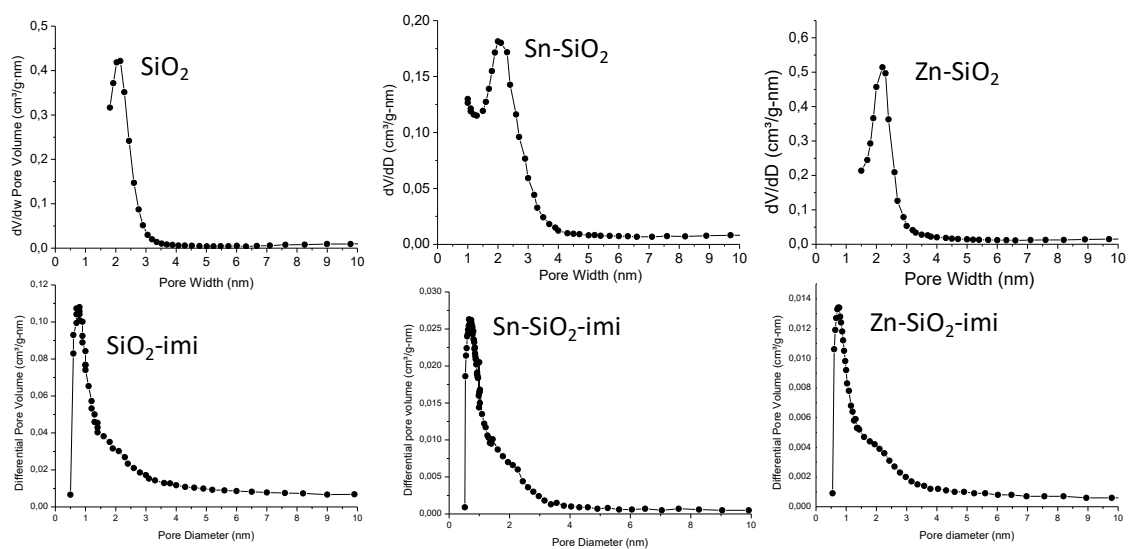
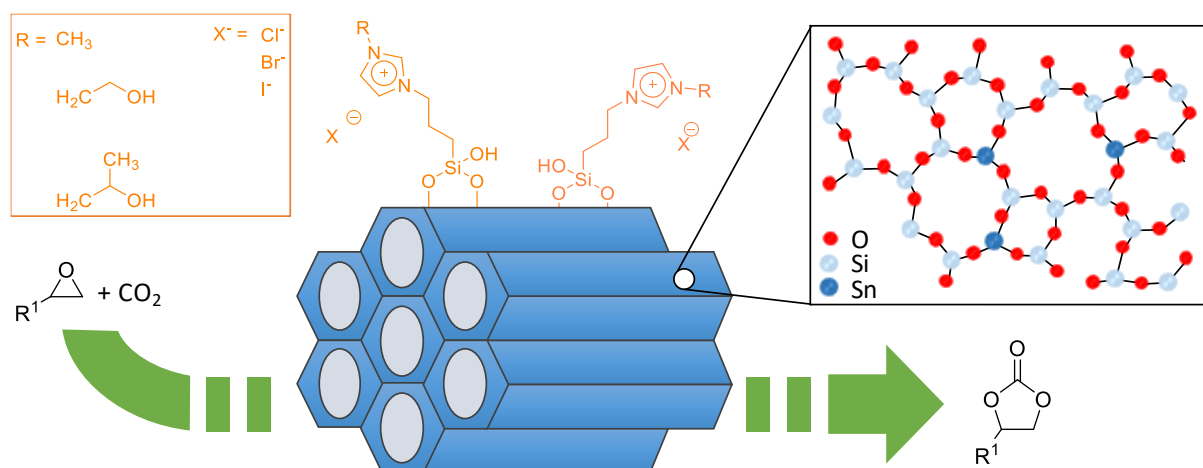


Figure S2: Pore size distribution of SiO_2 ; Sn-SiO_2 and Zn-SiO_2 determined by BJH method and $\text{SiO}_2\text{-imi}$; $\text{Sn-SiO}_2\text{-imi}$ and $\text{Zn-SiO}_2\text{-imi}$ determined by HK method.

Chapter II

Multifunctional heterogeneous catalysts highly performing in the conversion of carbon dioxide: mechanistic insights



Abstract

A series of novel multi-functional heterogeneous catalysts was efficiently synthesized. Spherical silica nanoparticles embedding Sn as single site (**Sn-SiO₂**) were prepared via a straightforward and time-saving procedure. The silica surface was selectively decorated with two different imidazolium-based moieties bearing primary or secondary alcohols in order to investigate if the presence of two co-catalysts (Lewis acid site and alcohol functionality) may induce a synergic activation improving the overall catalytic performances. The solids were fully characterized through ¹¹⁹Sn, ²⁹Si and ¹³C solid state NMR as well as via N₂ physisorption, transmission electron microscopy, ICP-OES and combustion chemical analysis. FT-IR of CO₂ adsorption was employed to obtain some mechanistic insights on the interactions between CO₂ and the surface of the novel solids. All the synthesized catalysts were compared selecting the challenging CO₂ fixation on either cyclohexene oxide or styrene oxide to produce the corresponding cyclic carbonates. The best solids display excellent catalytic performances outcompeting with other totally heterogeneous catalysts previously reported in the literature. Finally, the true heterogeneous nature of the catalyst was proved in consecutive catalytic cycles. The characterization of the material after reuses allowed confirming the stability of the solid under the selected reaction conditions.

The results presented in this chapter have been published in:

A. Comès, S. Fiorilli, C. Aprile, Multifunctional heterogeneous catalysts highly performing in the conversion of carbon dioxide: Mechanistic insights, *Journal of CO₂ Utilization*, 37 (2020) 213-221.

Introduction

In the previous chapter, the synthesis of a bi-functional solid was reported. The insertion of both Zn and Sn in the silica framework brought the Lewis acidity, useful for the conversion of CO₂. The materials were post-functionalized with an imidazolium chloride and demonstrated an enhanced activity compared to the metal-free mesoporous silica. Herein, a different approach was selected. The best catalyst (identified in the previous chapter) was employed as support and the solid was functionalized with two different imidazolium-based moieties bearing primary or secondary alcohols instead of the previously employed N-methylimidazolium. The idea was to investigate the activation by an alcohol as H-bond donor in addition to the one of the Sn as Lewis acid.

To the best of our knowledge there are very few reports in which the use of a tri-functional heterogeneous catalysts (catalysts plus both Lewis acid and alcohol moieties as co-catalyst) is envisaged. This lack of examples of tri-functional catalytic systems can be justified by the generally accepted reaction mechanism. According to this mechanism, the interest of having alcohols or Lewis acid site is related to the easier opening of the 3-member ring, hence the double presence of both co-catalysts should be redundant.

However, the activation of CO₂ should be also considered. It is known,[140] that the oxygen atoms of this small molecule display a Lewis base character and can coordinate to Lewis acid sites such as metal centres (e.g. Zn, Ni), leading to a more electrophilic carbon atom. This coordination has been proved on various metal centres and complexes and the resulting enhanced electrophilicity was demonstrated by ¹³C-NMR and IR measurements.[140, 141]

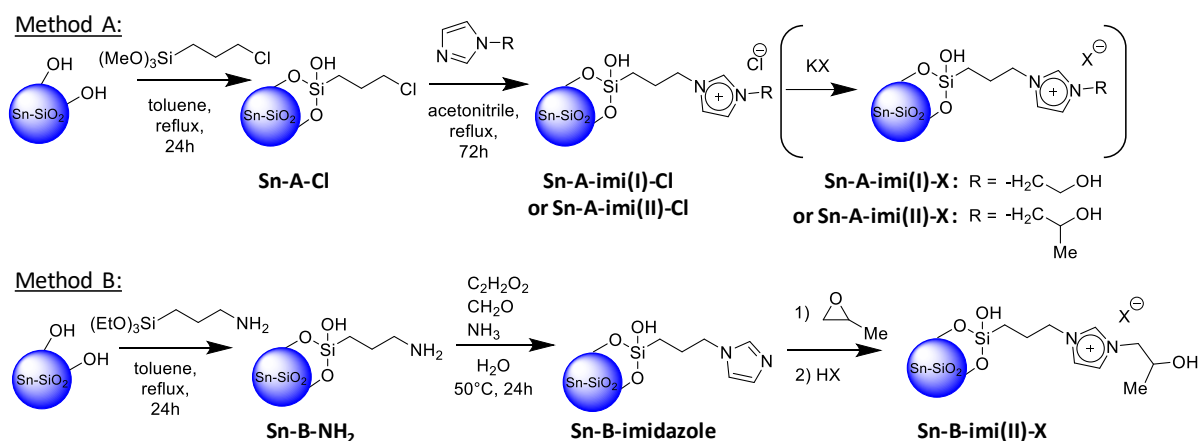
Here we present for the first time the synthesis of a tri-functional heterogeneous catalyst bearing imidazolium salts decorated with alcohol functionalities anchored on a porous support embedding Sn as single site to play the role of acid centre. The materials were fully characterized via different techniques including N₂ physisorption, ¹³C and ²⁹Si NMR, transmission electron microscopy. FT-IR of CO₂ adsorption was employed to obtain some mechanistic insights on the interactions between CO₂ and the surface of the novel heterogeneous catalysts. The possible synergistic activation of the two co-catalysts was investigated. The best solid displayed excellent catalytic performances, better than the analogue bi-functional solids as well as than other reference catalysts reported in the literature. Furthermore, this fully heterogeneous material was reused in several catalytic cycles thus confirming its stability under the selected reaction conditions.

Results and Discussion

Spherical silica nanoparticles embedding Sn as single site (**Sn-SiO₂**) were prepared via a straightforward and time-saving procedure previously reported by our research group.[16, 19] Herein, the silica surface was selectively decorated with two different imidazolium-based moieties bearing primary or secondary alcohols in order to investigate if the presence of two co-catalysts (Lewis acid site and alcohol functionality) may induce a synergistic activation enhancing the overall catalytic performances.

A first series of materials, depicted in Scheme 1 (Method A), was successfully prepared reacting the surface of **Sn-SiO₂** with 3-chloropropyltrimethoxysilane followed by the nucleophilic substitution of the selected imidazole derivative on the terminal carbon of the alkyl chain.[210] Two imidazolium-based solids, bearing primary or secondary alcohols (respectively labelled as **Sn-A-imi(I)-Cl** and **Sn-A-imi(II)-Cl**) were obtained. A post-synthesis metathesis allowed preparing the analogous Br⁻ and I⁻ derivatives. For the sake of comparison, a set of materials without Sn inserted in the silica matrix was synthesized as well and labelled as **SiO₂-A-imi(I)-Cl** and **SiO₂-A-imi(II)-Cl**.

A second series of solids, depicted in Scheme 1 (Method B), was prepared employing an alternative method to generate the catalysts bearing an imidazolium unit functionalized with a secondary alcohol (**Sn-B-imi(II)-Cl**). In this procedure, the surface of the porous solid was functionalized via reaction with 3-aminopropyltriethoxysilane. Hence, the imidazole moiety was synthesized in situ through the Debus-Radziszewski reaction.[211-213] Finally, the ring opening of propylene oxide, followed by acidic treatment allowed generating the final **Sn-B-imi(II)-Cl** material.[214] The advantage of this approach stands in the possible generation of a library of imidazolium-based solids employing **Sn-B-imidazole** as a key intermediate, avoiding the prior synthesis and purification of the desired imidazole derivative and a time-consuming quaternization on the 3-chloropropyl moiety. Moreover, the analogous materials bearing bromide or iodide as counterion were prepared simply varying the acid used in the last step, avoiding the final anion exchange step, like in Method A, or the initial use of the 50 times more expensive 3-bromopropyltrimethoxysilane or 3-iodopropyltrimethoxysilane.



Scheme 1: Multi-step functionalization of silica matrices using two different methods. $X^- = Cl^-, Br^-, I^-$

All the materials were deeply characterised through various techniques including solid-state ^{119}Sn NMR, ^{13}C -CPMAS-NMR, N_2 physisorption, transmission electron microscopy, FT-IR spectroscopy. ^{13}C NMR spectra (Figures 1 and S1-2) exhibited the two characteristic peaks at 122 and 137 ppm corresponding to the aromatic carbon of the imidazolium ring together with the signals in the aliphatic region corresponding to the carbon atoms of the linker as well as of the imidazolium modified alkyl chain. The ^{13}C NMR spectra of the intermediate solids (**Sn-A-Cl**; **Sn-B-NH₂** and **Sn-B-imidazole**) together with the final materials bearing Br^- and I^- as counterions are reported in Supporting Information (Figures S1-2). It worth to note the three clearly distinguishable peaks in the aromatic region of **Sn-B-imidazole**. The anchoring of the organic moiety on the silica surface was verified via solid-state ^{29}Si -CPMAS-NMR experiments. The presence of two signals (Figures 2 and S3) at -65 and -58 ppm which can be ascribed respectively to $-\text{CH}_2-\text{Si}(\text{OSi})_3$ (T^3) and $-\text{CH}_2-\text{Si}(\text{OSi})_2(\text{OH})$ (T^2) species allowed confirming the covalent nature of the functionalization.

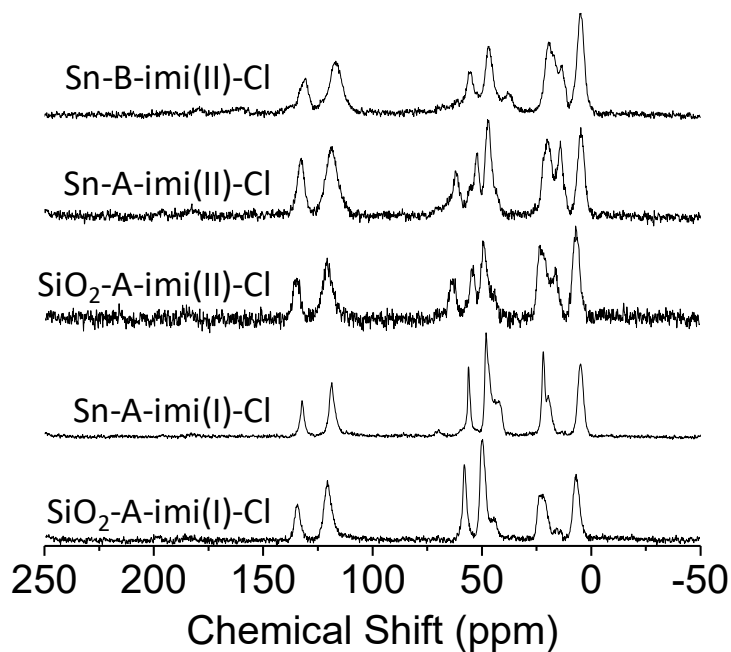


Figure 1: ^{13}C -CP-MAS-NMR spectra of the materials

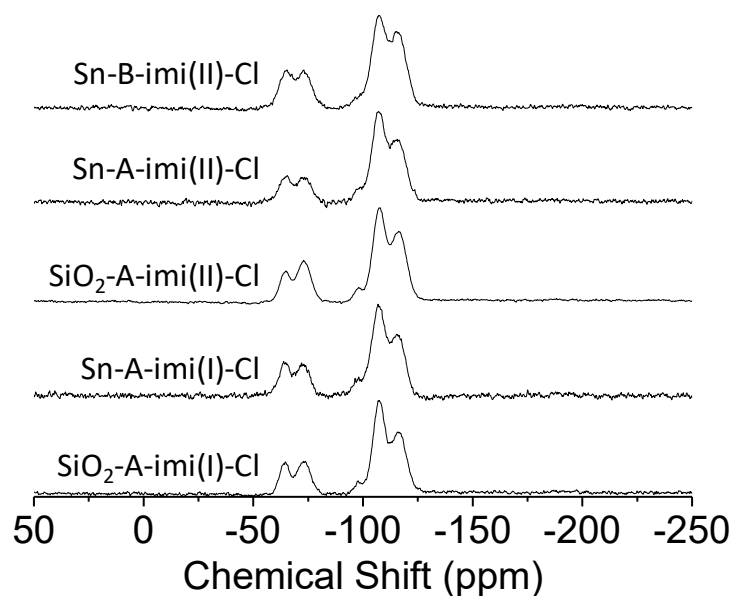


Figure 2: ^{29}Si -CP-MAS-NMR spectra of the materials

The loading of imidazolium salt was quantified via combustion chemical analysis while the amount of Sn inserted in the structure (Table 1) was determined via Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

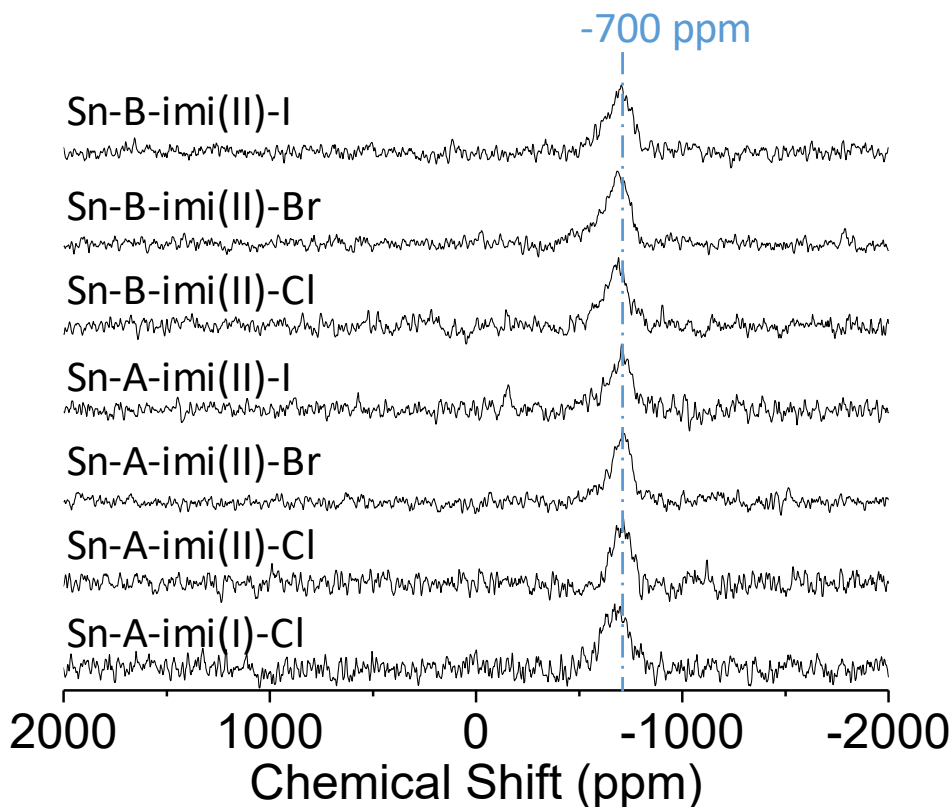


Figure 3: ^{119}Sn solid state NMR spectra. Vertical guideline centred at -700 ppm

^{119}Sn -NMR spectroscopy under static conditions revealed the presence of one band centred at -680 ppm thus confirming the insertion of Sn as single site (Figure 3). However, due to the broad nature of the signal, the presence of traces of extra-framework SnO_2 species (centred at -600 ppm) cannot be completely excluded. It is known that the isomorphic substitution of Si with Sn in the SiO_2 architecture will provide the Lewis acidity needed to co-activate the conversion of carbon dioxide.[19, 25, 197, 210] However, in order to investigate the presence of a possible synergic co-activation of CO_2 molecules on Sn centres at the surface, an in-depth FT-IR investigation on selected samples was performed. Three solids, **Sn-SiO₂**, **SiO₂-A-imi(II)-Cl** and **SiO₂-A-imi(I)-Cl**, were selected to understand and discriminate the possible different contributions coming from the interaction occurring between CO_2 and the surface sites. Figure 4a shows the difference spectra of CO_2 dosages on **Sn-SiO₂**. As widely reported in the literature,[215] the main component at 2344 cm^{-1} can be easily ascribed to the CO_2 molecules interacting with Si-OH groups at the amorphous silica surface. The band for lower coverage (i.e. pink curve) is slightly asymmetric, showing a shoulder at higher frequency. This component (at around 2350 cm^{-1}) was tentatively ascribed to the molecule probing sites with slightly higher acidity compared to silanols species, i.e. OH groups interacting with intra-framework Sn sites.

The difference spectra of CO₂ on **SiO₂-A-imi(II)-Cl** (Figure 4b) displays a main component at lower frequency (2339 cm⁻¹) compared with that reported for **Sn-SiO₂** and even lower than that reported for the molecule interacting with silicalite surface (2341 cm⁻¹). The observed component can be ascribed to physisorbed CO₂, unspecifically interacting with a solid surface. More in detail, the signal could be assigned to CO₂ molecules adsorbed within the silica mesopores, whose size are expected to be reduced as consequence of the functionalization, and slightly perturbed by the electrostatic interactions with pore walls. The absorption band results slightly asymmetric for low CO₂ coverage, most likely due to a component of weak intensity at around 2344-2345 cm⁻¹, due to molecules probing residual OH species. On the contrary, no component at higher frequency is discerned, which further supports the previous assignation since for the SiO₂-A-imi(II)-Cl solid (without Sn), no Lewis acidity is expected. **SiO₂-A-imi(I)-Cl** shows (Figure 4c) a very similar spectrum characterized by a main component at 2339 cm⁻¹ due to physisorbed CO₂, unspecifically interacting with the surface as well as by the absence of additional bands at higher frequencies. The component at 2344 cm⁻¹ displays in this case a slightly higher intensity compared to the previous spectrum, which could result from the higher accessibility of the surface hydroxyl groups as consequence of the lower steric hindrance of the imidazolium functionalities or, in alternative, to a slightly lower degree of surface functionalization.

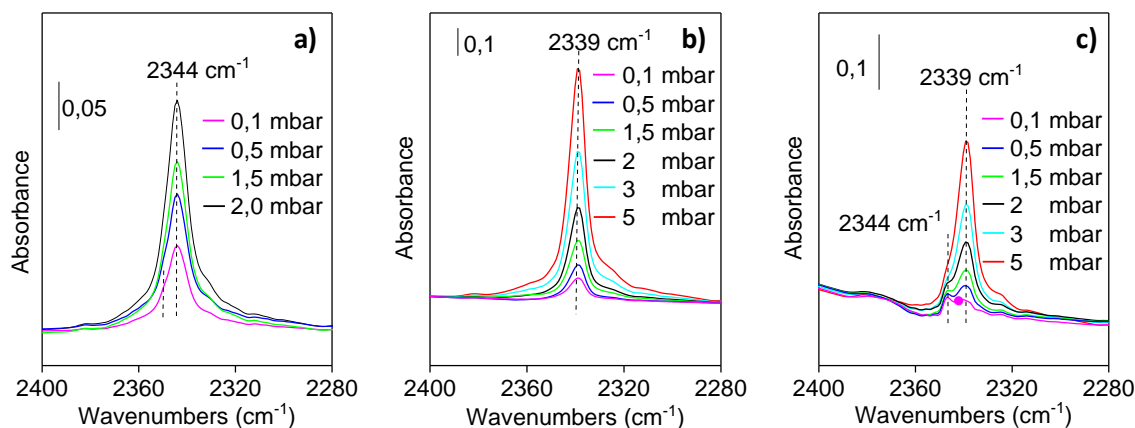


Figure 4: Difference FT-IR spectra of CO₂ dosages on a) Sn-SiO₂; b) SiO₂-A-imi(II)-Cl and c) SiO₂-A-imi(I)-Cl

The spectroscopic characterization clearly highlighted that CO₂ is able to interact with the surface Sn centres acting as Lewis acid sites. However, in order to understand if this interaction could also occur on the tri-functional catalysts, FT-IR spectra of CO₂ adsorbed on **Sn-A-imi(II)-Cl** was performed as well and the related difference spectra are reported in Figure 5. The component at around 2352 cm⁻¹ can be tentatively ascribed to linear adduct of CO₂ linearly

coordinated to Lewis acidic sites.[216] This value is higher than the values generally ascribed to CO₂ interacting with Brönsted sites,[217] also for bridged OH of protonic zeolites (2344-2345 cm⁻¹), therefore it is reasonable that it arises from the interaction of the molecule with unsaturated Sn sites, which upon imidazolium functionalization and consequent consumption of surface OH groups, result more exposed and thus prone to react compared to unfunctionalized **Sn-SiO₂** sample.

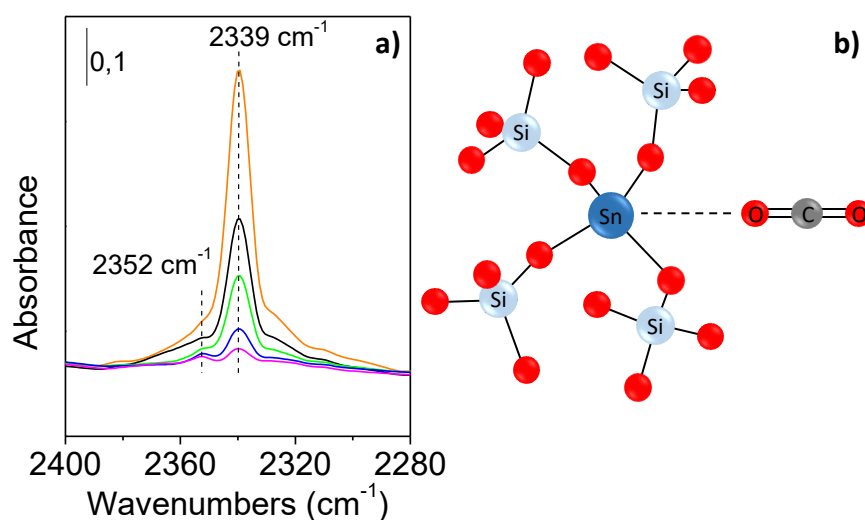


Figure 5: Difference FT-IR spectra of CO₂ dosages on Sn-A-imi(II)-Cl (a) and schematic representation of CO₂ interacting with Sn (b)

Table 1: Textural and structural properties of the synthesized materials

Material	Amount of imidazolium ^a (mmol/g)	Amount of Sn ^b (mmol/g)	BET surface area (m ² /g)	Pore size distribution ^c (nm)
SiO ₂ -A-imi(I)-Cl	0.917	-	353 ± 4	2.0
Sn-A-imi(I)-Cl	0.655	0.140	544 ± 3	2.4
SiO ₂ -A-imi(II)-Cl	0.946	-	356 ± 4	2.2
Sn-A-imi(II)-Cl	0.787 - 0.858	0.126	480 ± 4	2.4
Sn-A-imi(II)-Br	0.689	0.153	479 ± 3	2.5
Sn-A-imi(II)-I	0.635	0.147	447 ± 4	2.3
Sn-B-imi(II)-Cl	1.02	0.124	467 ± 4	2.4
Sn-B-imi(II)-Br	0.923	0.156	327 ± 4	2.3
Sn-B-imi(II)-I	0.842	0.136	375 ± 5	2.4

^a Range of imidazolium salt determined via combustion chemical analysis. Amount estimated considering the nitrogen percentage. ^b Amount of Sn determined via inductively coupled plasma optical emission spectroscopy (ICP-OES). ^c Pore size distribution calculated using DFT method, cylinder geometry, model N₂ – cylindrical pores – oxide surface – regularization 0.10 – version 2 deconvolution. See Experimental section for more details.

Relevant parameters in heterogeneous catalysis are represented by the specific surface area and pore size distribution. The textural properties of the solids were investigated via nitrogen physisorption analysis. All materials displayed an elevated surface area (Table 1) and a type IV isotherm, typical of MCM-41-like systems with a hysteresis loop at high relative pressure (Figures 6 and S4-5). This behaviour can be ascribed to the disordered meso-macroporous network formed as consequence of the inter-particles aggregation due to the extra-small size of the particle.[16, 18] The determination of the pore size distribution in the functionalized solids required particular attention. The Barrett, Joyner and Halenda (BJH) method, usually employed for the evaluation of the mesopores dimensions, failed in our case most probably because, after functionalization, the pore diameter decreased entering in the region of the micropores or at the boundary between meso- and micropores. In literature, the Horvath-Kawazoe (HK) approach is often proposed as alternative method to estimate the pore size distribution (psd) of microporous carbon and other microporous solids.[218] However, its use

is sometimes questioned when applied to ordered materials as zeolites and MOF.[219] Recently, mathematical modelling using a density functional theory (DFT) started to be widely employed since it represents the only method enabling the evaluation of both micro- and mesoporosity.[219-221] Hence, a DFT analysis was applied to all the imidazolium-based solids and, for the sake of comparison, to the non-functionalized analogues (Figures 6 and S4-5). As expected, the functionalization with organic moieties caused a clear decrease of the psd.

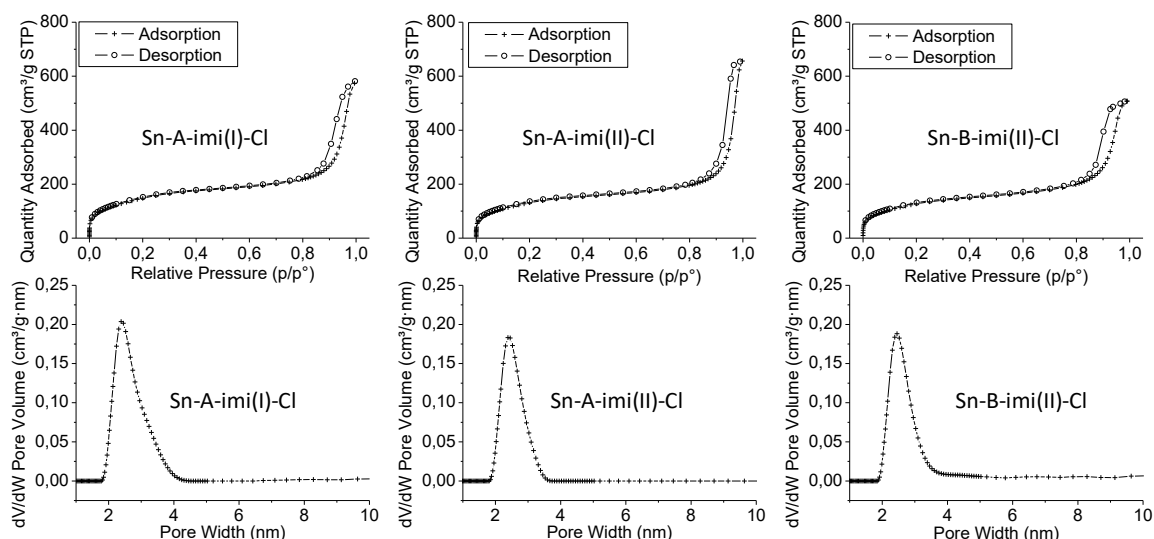


Figure 6: N_2 physisorption isotherms (top) and pore size distribution (down) of Sn-A-imi(I)-Cl; Sn-A-imi(II)-Cl and Sn-B-imi(II)-Cl

This finding also confirms the possible confinement effect of CO_2 molecules within the pores as observed during the FT-IR measurements (band at 2339 cm^{-1}).

The extra small size of the particles was also confirmed via transmission electron microscopy (TEM) measurements (Figures 7 and S6). All the particles display an almost spherical shape and a particle size distribution below 100 nm. As expected, the functionalization with the organic moieties did not alter the morphology of the particles.

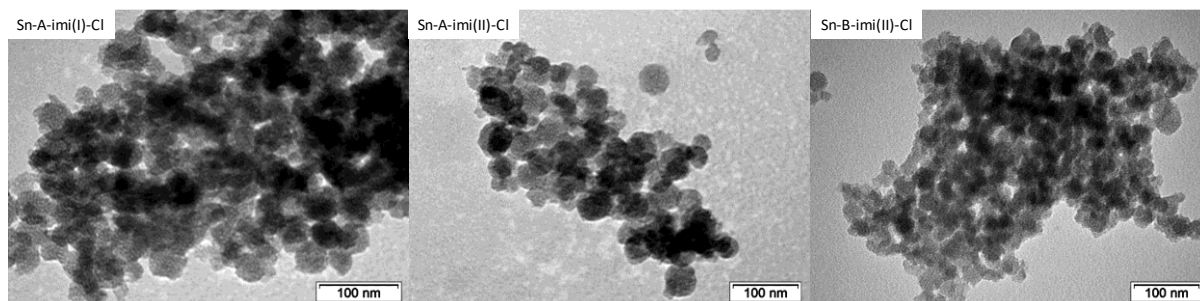


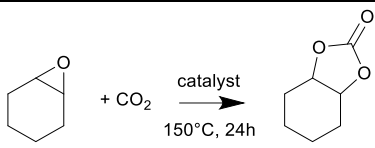
Figure 7: TEM images of Sn-A-imi(I)-Cl ; Sn-A-imi(II)-Cl and Sn-B-imi(II)-Cl

All the solids exhibited the expected structure as well as interesting textural features for catalytic applications. Hence, they were tested in the conversion of CO_2 selecting the

challenging cyclohexene oxide (Table 2) as initial benchmark. In order to allow a meaningful comparison, the activity of the solids was compared in terms of turnover number (TON, here defined as moles of epoxide converted/moles of imidazolium salt). Under the selected conditions (Table 2) **Sn-A-imi(I)-Cl** displayed higher TON than its Sn-free homologue **SiO₂-A-imi(I)-Cl** (compare Entries 1 and 2) as well as of the tin silicate decorated with methylimidazolium moieties **Sn-A-imi-Cl** (Entry 3) thus demonstrating the positive influence of the presence of both the Lewis acidity and alcohol functionalities.

To further support this statement an additional experiment was performed (Entry 4) employing **Sn-A-imi-Cl** and the equimolar amount (respect to the imidazolium) of ethanol. The slightly improved TON obtained in this case compared to the one achieved using **Sn-A-imi(I)-Cl** catalyst can be attributed to the presence of ethanol under homogenous conditions. The comparison between the catalysts **Sn-A-imi(II)-Cl** and **SiO₂-A-imi(II)-Cl** (Entries 5-6) allows confirming further the synergy activation due to the presence of two co-catalysts. Based on the previous IR investigation we may envisage a mechanism in which CO₂ molecules could be activated by the Sn centres while the epoxides would interact either with Sn (via Lewis acid-base interaction) or with the OH groups (via H-bond formation) at the imidazolium moieties. Moreover, the catalytic tests demonstrated the higher efficiency of the materials containing secondary alcohols.[145] The better performances in terms of TON of **Sn-A-imi(II)-Cl** compared with **Sn-A-imi(I)-Cl**, despite the slightly higher surface area of the latter, could be ascribed to the easier interaction of the primary alcohol with the more accessible silanols presents at the silica surface. This “intra-molecular” interaction would render the primary alcohol less available to react with the epoxides. The material synthesized following the method B was tested as well (Entry 7). Surprisingly, the **Sn-B-imi(II)-Cl** showed lower conversion and TON than the analogous materials prepared through method A (compare Entries 5 and 7). The decreased catalytic performances could arise from a non-complete functionalization through the Debus-Radziszewski reaction. A careful look at the ¹³C-CPMAS-NMR (Figure 1) reveals the presence of a minor contribution at 45 ppm which can be due to the presence of unreacted aminopropyl functionalities.

Table 2: Conversion of cyclohexene oxide into the corresponding cyclic carbonate with use of different catalysts ^a

				
Entry	Catalyst	Conv. (%)	Sel. (%)	TON ^b
1	Sn-A-imi(I)-Cl	21	>95	155
2	SiO ₂ -A-imi(I)-Cl	19	>95	98
3	Sn-A-imi-Cl	26	>95	90
4	Sn-A-imi-Cl ^c	39	>95	174
5	Sn-A-imi(II)-Cl	36	>95	197
6	SiO ₂ -A-imi(II)-Cl	33	>95	155
7	Sn-B-imi(II)-Cl	27	>95	128

^a Reaction conditions: Cyclohexene oxide (24.0 mL; 237 mmol), mass of catalyst (500 mg), CO₂ initial pressure (25 bar), temperature (150 °C), time (24 h), 500 rpm. ^b Turnover number (TON) calculated as moles of epoxide converted/moles of imidazolium sites. Amount of imidazolium salt quantified via combustion chemical analysis for each catalyst. ^c Reaction performed in presence of 1 equivalent of EtOH (30.8 μL, 0.527 mmol)

The solid displaying the best performances was selected to challenge the true heterogeneous nature of the catalyst. Styrene oxide was employed to test the recyclability of the **Sn-A-imi(II)-Cl** catalyst (Figure 8). The reaction was performed at 125 °C. After each cycle, the solid was recovered from the reaction mixture by centrifugation, washed and reused. A slight decrease of the activity with the cycles followed by a stabilization was observed. However, an additional washing procedure in presence of 50 mL ethanol acidified with 1 mL fuming HCl solution after the fourth cycle allows restoring completely the catalytic activity. The characterisation of the solid after reuse was performed as well thus confirming the stability of the catalyst under the selected conditions (Figures S7-10).

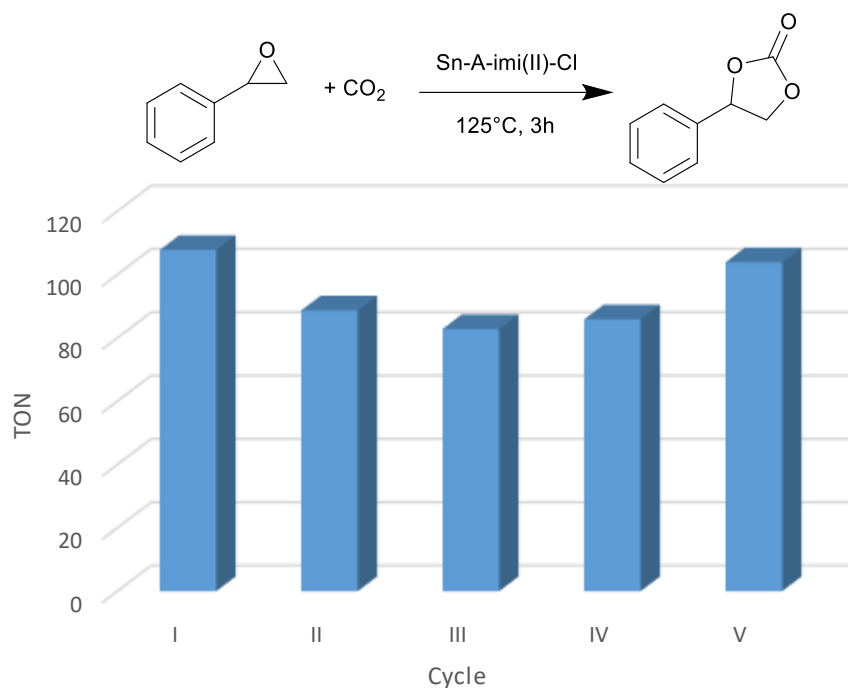


Figure 8: Catalytic performance of Sn-A-imi(II)-Cl in subsequent reaction cycles

It is well known that the counterion of the imidazolium salt is of primary importance[222, 223] since it is the active catalyst opening the 3-membered ring epoxide via nucleophilic substitution (S_N2) as well as the leaving group enabling the formation of 5-membered cyclic carbonate.[47, 132, 224] An anion exchange was performed on **Sn-A-imi(II)-Cl** using an aqueous solution of KBr or KI to generate respectively **Sn-A-imi(II)-Br** and **Sn-A-imi(II)-I**. Catalytic tests over styrene oxide (Table 3) demonstrated that enhanced TON can be easily achieved just selecting the appropriate counterion (compare Entries 1-3 in Table 3). Analogous experiments performed in presence of the materials obtained via the method B (Entries 4-6), confirmed the improved performance of the I⁻ containing solids and proved that in presence of more reactive nucleophiles the difference between the catalysts prepared employing the method A or B is less evident. Despite the lower activity of the catalysts prepared via the method B, this strategy remains attractive for the easy preparation of a library of imidazolium-based. The enhanced efficiency related to the counterion is also evidenced by a monitoring of the CO₂ consumption over time presented in Figure 9. To challenge even more our catalyst, additional catalytic tests at the temperature of 80 °C and 50 °C and in presence of epichlorohydrin and glycidol respectively were performed as well. From the table (Entries 7 and 8) emerged that **Sn-A-imi(II)-Cl** displays excellent catalytic performances also at low temperature evidenced by TON up to 247. A further test (Entry 9) at a lower pressure (10 bar) clearly shows that the catalytic activity of the **Sn-A-imi(II)-Cl** solid is not strongly influenced by this pressure

Table 3: Conversion of epoxide into the corresponding cyclic carbonate with use of different catalysts ^a

Entry	Catalyst	Substrate	Temp. (°C)	Conv. (%)	Sel. (%)	TON ^b	TON _M ^c
1	Sn-A-imi(II)-Cl	Styrene oxide	125	22	>95	108	735
2	Sn-A-imi(II)-Br	Styrene oxide	125	36	>95	214	991
3	Sn-A-imi(II)-I	Styrene oxide	125	69	>95	449	1976
4	Sn-B-imi(II)-Cl	Styrene oxide	125	10	>95	40	340
5	Sn-B-imi(II)-Br	Styrene oxide	125	40	>95	182	1080
6	Sn-B-imi(II)-I	Styrene oxide	125	63	>95	314	1950
7	Sn-A-imi(II)-Cl	Epichlorohydrin	80	14	>95	107	668
8 ^d	Sn-A-imi(II)-Cl	Glycidol	50	27	>95	247	1539
9 ^{d,e}	Sn-A-imi(II)-Cl	Glycidol	50	23	>95	209	1309

^a Reaction conditions: Substrate (24.0 mL), mass of catalyst (500 mg), CO₂ initial pressure (25 bar), time (3 h), 500 rpm. ^b Turnover number (TON) calculated as moles of epoxide converted/moles of imidazolium sites. ^c TON_M calculated as mole of epoxide converted/moles of Sn sites. Amount of Sn quantified via inductively coupled plasma optical emission spectroscopy (ICP-OES) for each catalyst. ^d Reaction time (6 h). ^e Constant pressure (10 bar)

decrease (compare Entries 8 and 9). This catalytic test highlights the excellent activity of the solid and indicates that milder reaction conditions can be employed without detrimental effect of the overall activity. It deserves to be mentioned that for these last catalytic essays the catalysts bearing the chloride as counterion was selected to challenge even more our catalytic system. Moreover, since in literature the TON values are often calculated considering the Lewis acid catalyst an additional series of turnover numbers (TON_M defined as moles of epoxide converted/moles of Sn) was also included in the table. As can be clearly seen in the table, our solids display outstanding TON_M, close to 2000 when I⁻ was used as counterion.

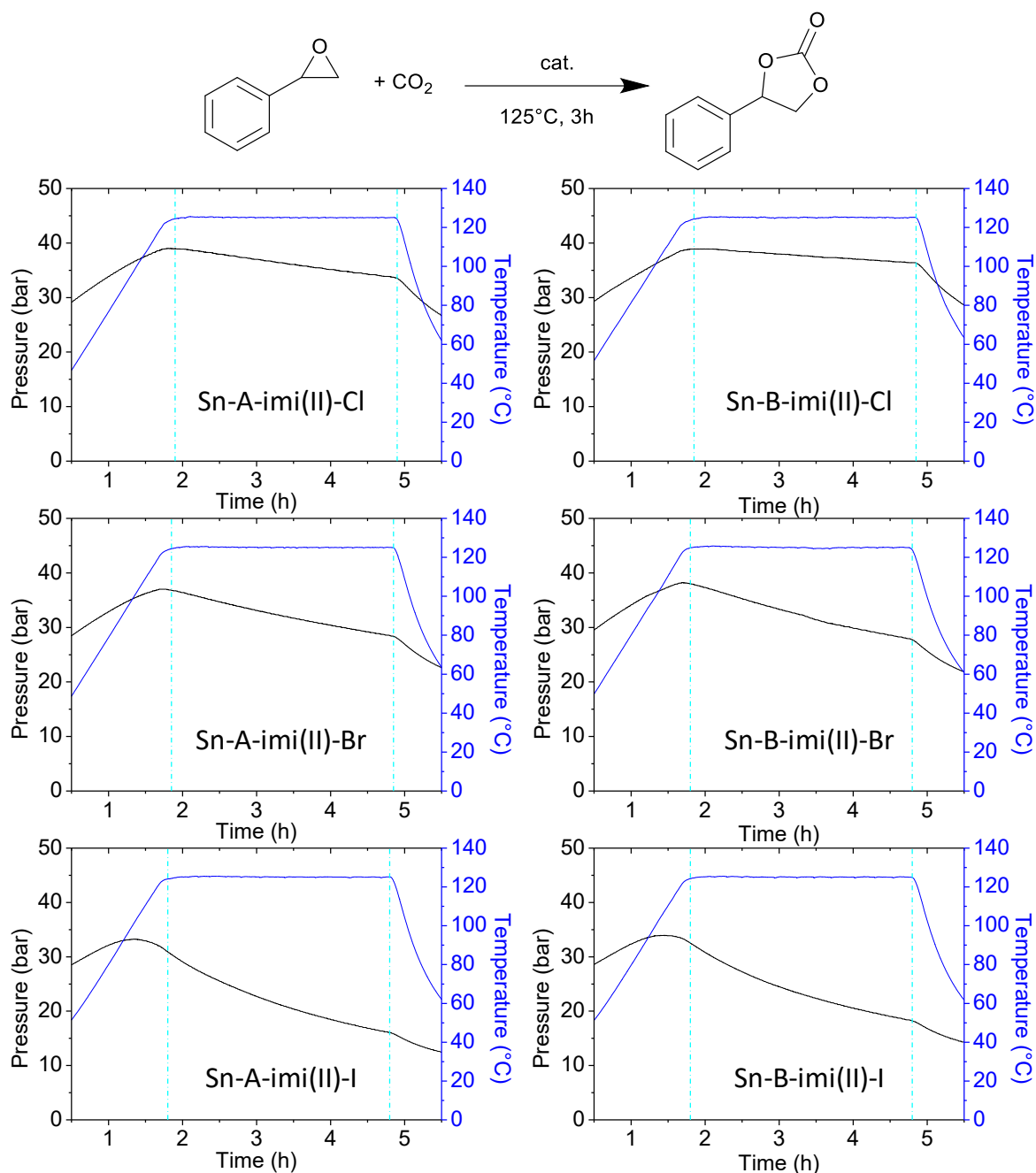


Figure 9: Monitoring of CO₂ pressure over time for some selected reactions. Vertical guidelines represent 3 h reaction time.

A comparison with other heterogeneous catalysts reported in literature was performed as well (Entries 4 to 7 in Table 4). It should be mentioned that a direct comparison with literature data is often difficult owing to the different reaction conditions employed for the catalytic tests. In our case this comparison is even more complicate since in many cases the catalytic tests employing a heterogeneous catalyst were performed in presence of an ammonium or imidazolium salt under homogeneous conditions.[147] The TON of our solids are much higher than other silica supported imidazolium salts previously reported (Entries 4-5) and tested in

Table 4: Conversion of styrene oxide into the corresponding cyclic carbonate with use of different catalysts

Entry	Catalyst	Temp. (°C)	Pressure (bar)	Time (h)	Conv. (%)	TON	Ref.
1	Sn-A-imi(II)-Cl	125	25	3	22	108	This work
2	Sn-A-imi(II)-Br	125	25	3	36	214	This work
3	Sn-A-imi(II)-I	125	25	3	69	449	This work
4 ^a	SiO ₂ - <i>p</i> -xylene-I	150	80	3	99	237	[47]
5 ^a	SiO ₂ - <i>p</i> -xylene-I	125	80	3	37	88	[47]
6 ^a	ZnTCPPC(Br)Etim-UiO-66	140	1	14	53	56	[183]
7 ^a	Catalyst 12-Br	90	10	6	80	40	[158]

^a Constant pressure

absence of co-catalysts. Moreover, our materials outcompete with other full heterogeneous bifunctional catalysts reported in literature as ZnTCPPC(Br)Etim-UiO-66, displaying imidazolium moieties and Lewis acid centres (Entry 6) or catalyst 12 prepared supporting a phosphonium salt decorated with a phenol moiety on silica (Entry 7).

Conclusions

A series of multifunctional catalysts bearing imidazolium-based moieties and both alcohol and Lewis acid functionalities as co-catalysts were efficiently synthesized and deeply characterized via a combination of various techniques including N₂ physisorption, ¹³C and ²⁹Si NMR, transmission electron microscopy, X-ray diffraction. FT-IR of CO₂ adsorption was employed to obtain some insights on the interactions between CO₂ and the surface of the novel heterogeneous catalysts.

The catalysts displayed excellent catalytic performances in the reaction between CO₂ and epoxides to give the corresponding cyclic carbonates hence proving that the presence of two

co-catalysts (Lewis acid site and alcohol functionality) may induce a synergic activation enhancing the overall catalytic performances. The performance of the solids was consistently correlated to physic-chemical data. The best solid catalyses efficiently the synthesis various of cyclic carbonates at low temperature and pressure down-to 50 °C and 10 bar respectively and it shows outstanding performances compared to other references catalysts reported in literature. Moreover, the true heterogeneous nature of the solids was tested via various recycles experiments.

Experimental

Materials and methods

Ammonium hydroxide (30 %), ammonia solution 4 M, glyoxal solution 40%, formaldehyde solution 37%, hydrochloric acid 2 M were purchased from Carl Roth GmbH+Co. Cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), N-methylimidazole, (3-chloropropyl)trimethoxysilane, hydriodic acid 57%, styrene oxide, epichlorohydrin, cyclohexene oxide, propylene oxide were purchased from TCI NV Europe. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, (3-aminopropyl)-triethoxysilane, potassium bromide, potassium iodide, imidazole, glycidol were purchased from Sigma-Aldrich Inc. 1-(2-Hydroxyethyl)imidazole, hydrobromic acid 47% were purchased from abcr GmbH. DMSO- d_6 was purchased from Eurisotop. All chemicals were used as received without further purification.

General procedure for the synthesis of SiO_2 and Sn- SiO_2 solids

Mesoporous silica based materials were prepared according to a dilute route.[19, 210] Ammonium hydroxide (1.42 mL, 10.95 mmol) and CTAB (1.52 g, 4.16 mmol) were dissolved in 726 mL of milli-Q water (18.2 M Ω .cm). When a clear solution was obtained, silica precursor TEOS (6.936 g, 33.29 mmol) and – if necessary – a solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (157.6 mg, 0.45 mmol) dissolved in 2 mL of ethanol were mixed together and added dropwise to the aqueous solution. After 1 h under stirring at room temperature, the solid was filtered and washed 3 times alternatively with water and ethanol. The solid was dried overnight at 60 °C and calcined under air for 8 h at 550 °C with heating and cooling rate of 2 °C/min.

Synthesis of 1-(2-Hydroxypropyl)imidazole

The synthesis was adapted from Borowiecki et al.[225] In a vial, 1 equivalent of imidazole and 1 equivalent of propylene oxide were mixed together, in solvent-free conditions. The vial was sealed and the mixture was stirred at 500 rpm and 32 °C for 16 h. The crude was purified via a water/ethyl acetate phase separation. The organic phase was dried over magnesium sulphate and the solvent was removed by evaporation under reduced pressure.

^1H -NMR (400 MHz, DMSO- d_6) δ : 0.96 (d, 3H), 3.76-3.88 (m, 3H), 4.90 (d, 1H), 6.82 (t, 1H), 7.02 (t, 1H), 7.54 (t, 1H). ^{13}C -NMR (400 MHz, DMSO- d_6) δ : 21.3; 53.9; 66.2; 120.6; 128.3; 138.2

General procedure for method A functionalization

The SiO₂ or Sn-SiO₂ solid was dried in oven at 100 °C overnight before functionalization. In a round bottom flask, the silica matrix (1.5 g) was suspended in 15 mL of dry toluene. Then, (3-chloropropyl)trimethoxysilane (12 mmol) was added. The mixture was stirred at reflux temperature for 24 h. After cooling, the functionalised solid was filtered and washed with ethanol. The solid was re-dispersed in 15 mL of acetonitrile. The imidazole derivative 1-(2-Hydroxyethyl)imidazole or 1-(2-Hydroxypropyl)imidazole was added and the mixture was stirred at reflux temperature for 72 h. After cooling, the material was washed with Soxhlet extractor using ethanol as solvent. A metathesis can further be performed to exchange the chloride anion. The solid was dried at 100 °C, immersed in saturated aqueous KBr or KI solution, dried at 100 °C and washed by distilled water.

The amount of imidazolium was evaluated through combustion chemical analysis. The efficiency of the metathesis was also verified by EDX analysis.

General procedure for method B functionalization

The SiO₂ or Sn-SiO₂ solid was dried in oven at 100 °C overnight before functionalization. In a round bottom flask, the silica matrix (1.5 g) was suspended in 15 mL of dry toluene. Under stirring, (3-aminopropyl)triethoxysilane (12 mmol) was added. The mixture was stirred at reflux temperature for 24 h. After cooling, the functionalised solid was filtered and washed by ethanol. The solid was re-dispersed in 3 mL NH₃ (4M). Glyoxal (1.371 mL 40% aqueous solution) and formaldehyde (0.894 mL 37% aqueous solution) were added and the reaction was stirred for 24 h at 50 °C. The solid became brownish. It was filtered and washed by ethanol. The solid was dispersed in ethanol in a round bottom flask. Propylene oxide (0.840 mL) was added and the reaction was stirred for 24 h at room temperature with a cap to avoid the propylene oxide to evaporate. Finally, 6 mL HCl (2 M) were added slowly and the mixture is stirred for 30 minutes. The solid was washed with a Soxhlet extractor using ethanol as solvent. The same procedure was performed using 1.377 mL HBr (47%) or 1.583 mL HI (57%) instead of HCl leading to a different anion for the imidazolium salt.

Supporting Information

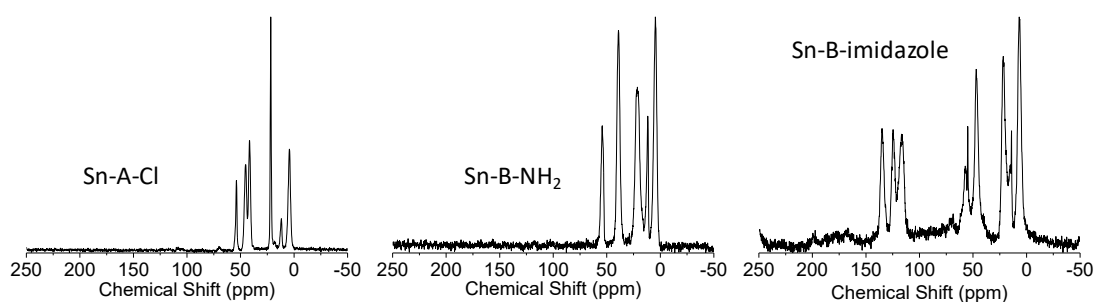


Figure S1: ^{13}C CP MAS NMR of the precursor materials.

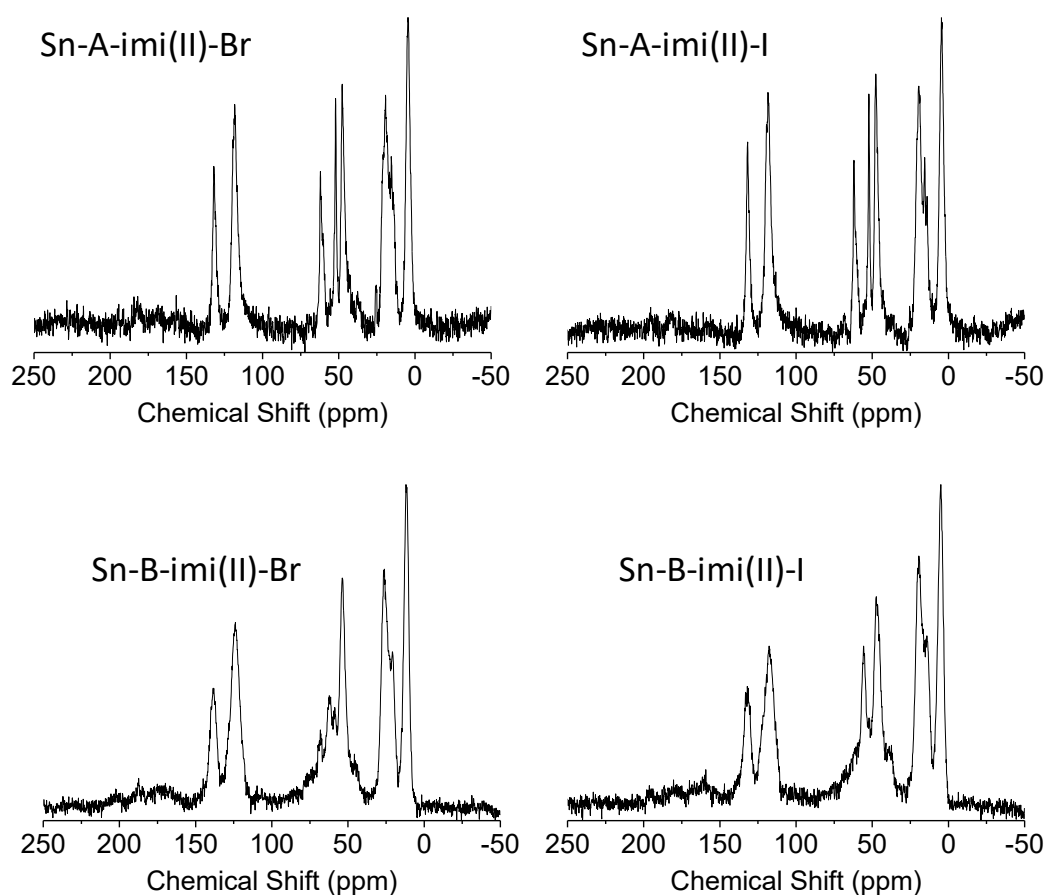


Figure S2: ^{13}C CP MAS NMR of the bromide and iodide containing materials

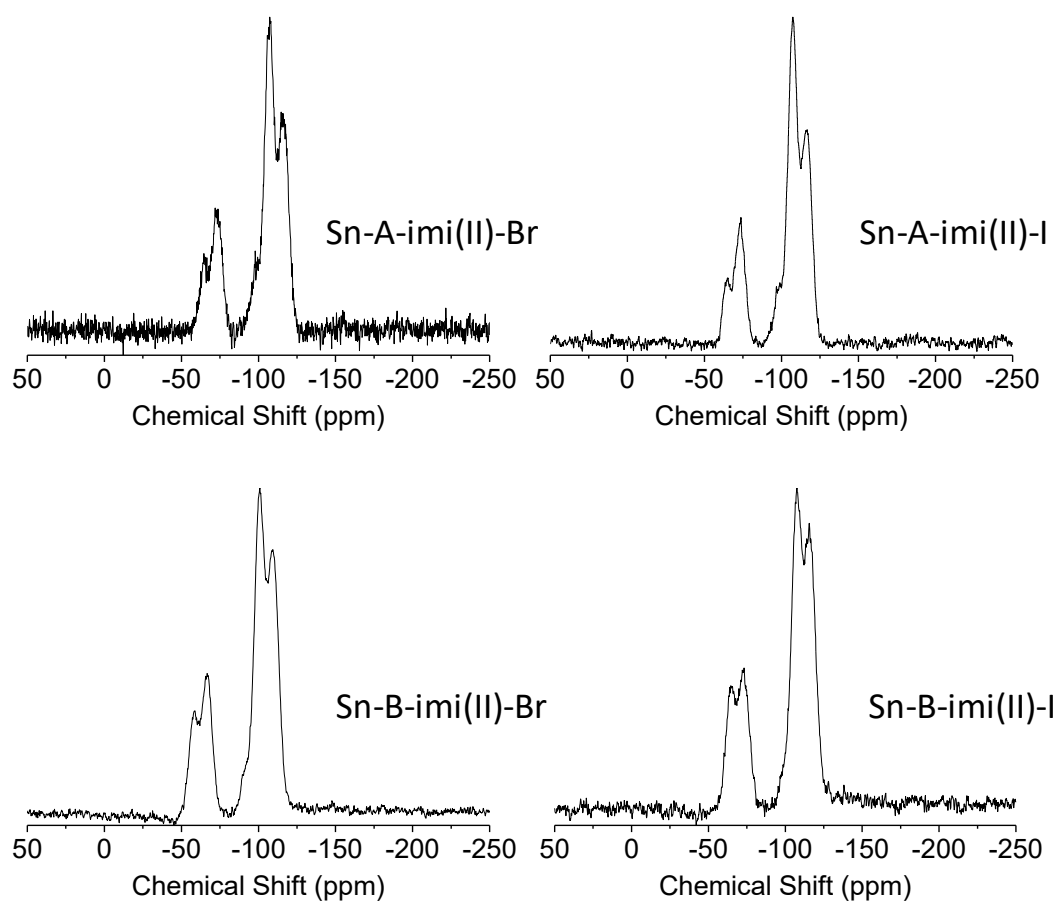


Figure S3: ^{29}Si CP MAS NMR of the bromide and iodide containing materials

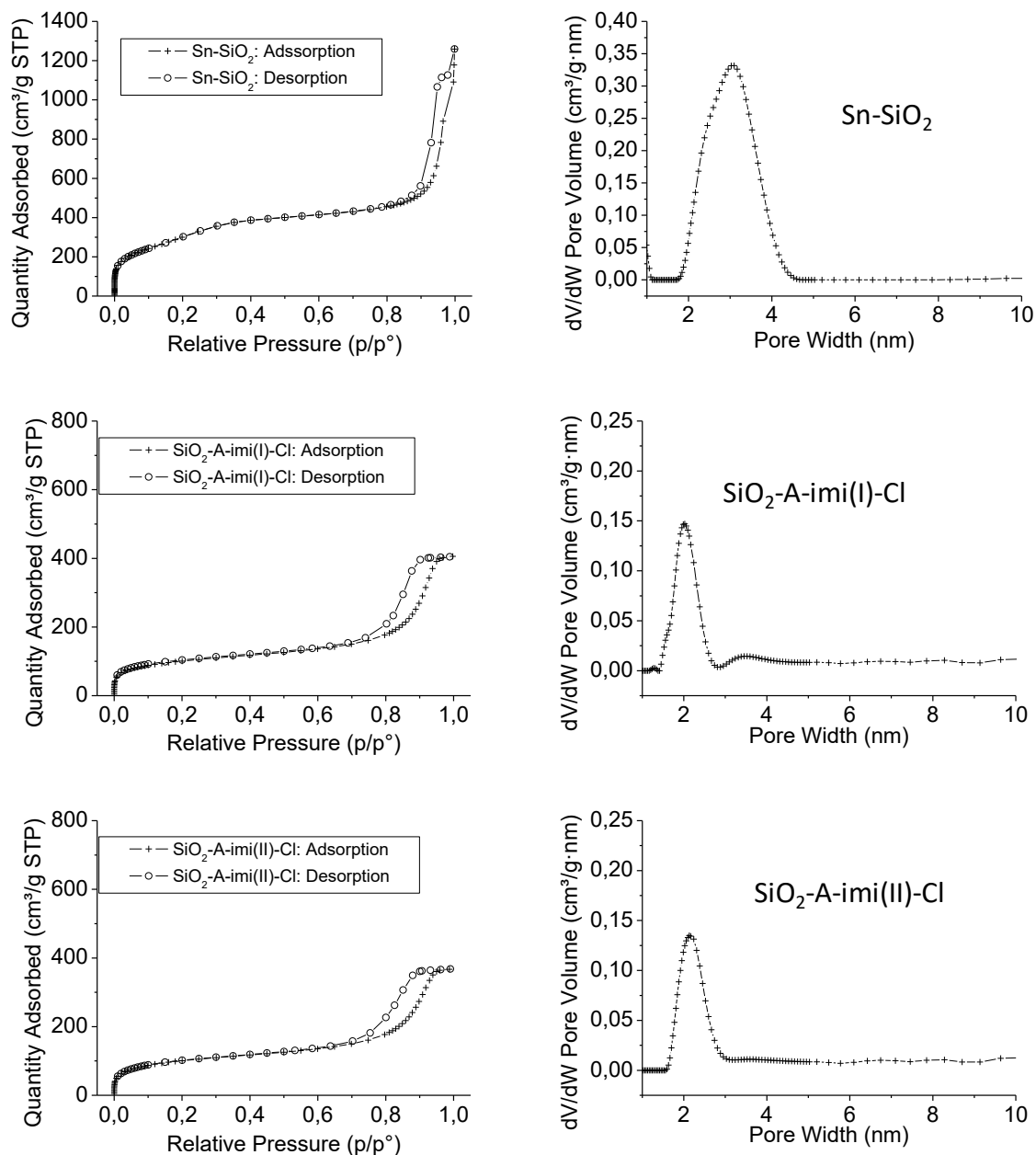


Figure S4: N₂ physisorption isotherms and the corresponding pore size distribution of non-functionalized and Sn-free materials

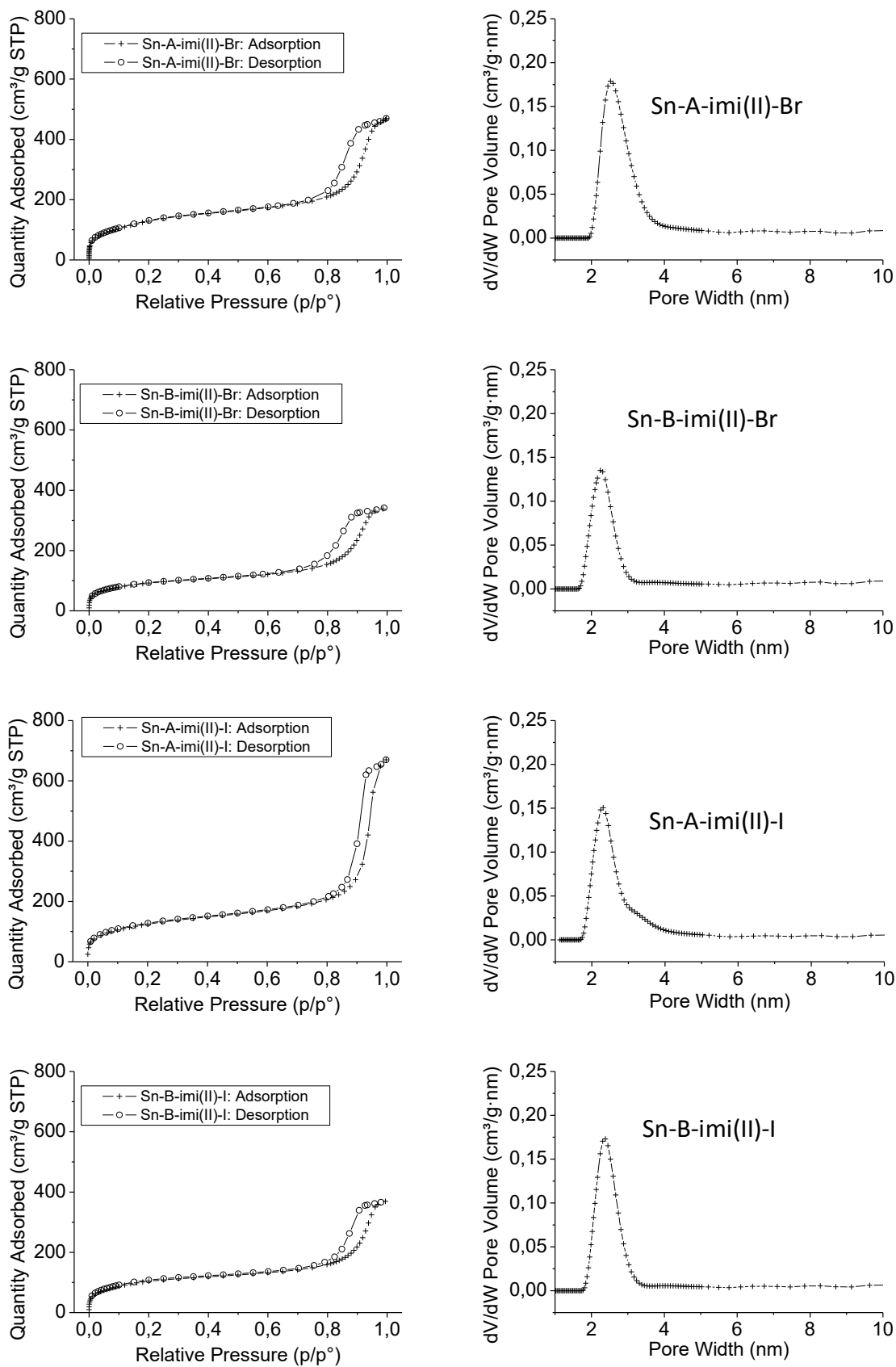


Figure S5: N₂ physisorption isotherms and the corresponding pore size distribution of the bromide and iodide containing catalysts

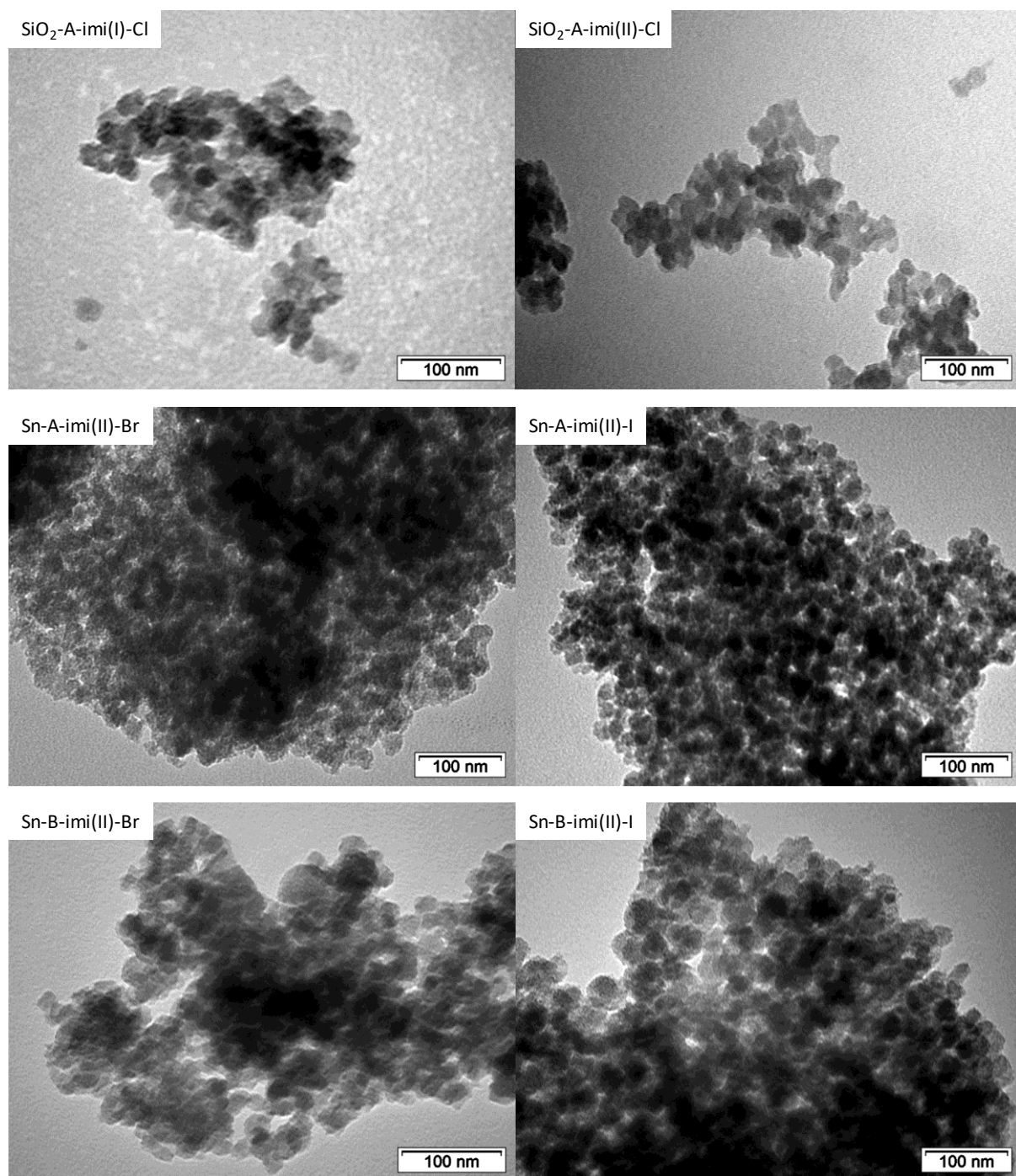


Figure S6: TEM pictures

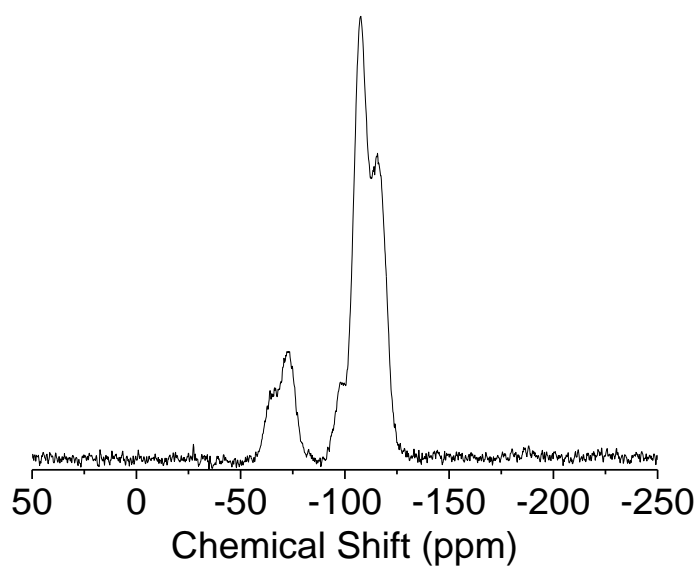


Figure S7: ^{13}C CP MAS NMR of Sn-A-imi(II)-Cl after 4th recycling test

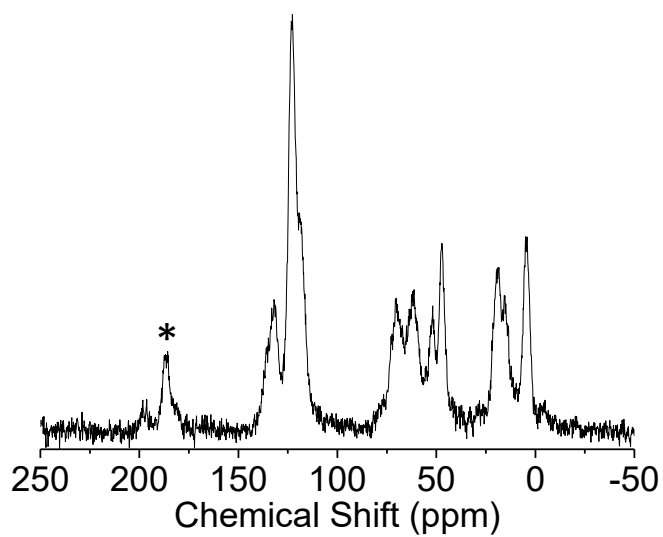


Figure S8: ^{29}Si CP MAS NMR of Sn-A-imi(II)-Cl after 4th recycling test

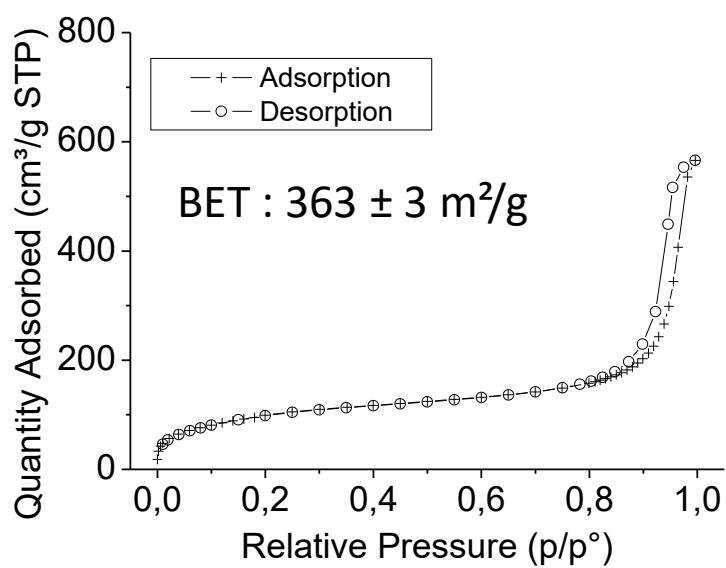


Figure S9: N_2 physisorption isotherm of Sn-A-imi(II)-Cl after 4th recycling test

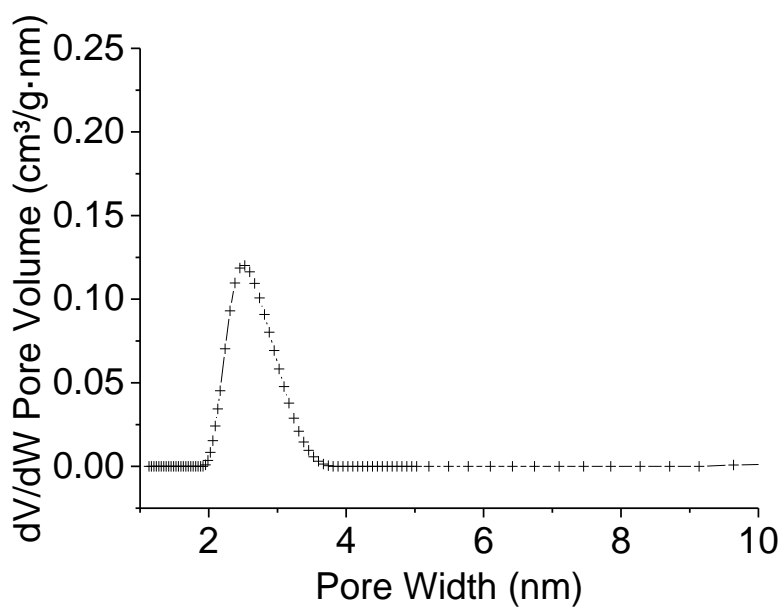


Figure S10: Pore size distribution of Sn-A-imi(II)-Cl after 4th recycling test

General conclusions

The present PhD thesis can be considered as a work in the general context of sustainable processes and synthesis strategies. Indeed, the concepts of Green Chemistry guided the present research to the development of new recoverable and reusable catalysts to promote a reaction itself consistent with Green Chemistry principles (see the last part of introduction section, dedicated to Green Chemistry within the frame of CO₂ conversion to cyclic carbonates).

Among the already available catalysts, imidazolium salts are among the mostly used and highly active for the conversion of epoxides and CO₂ to cyclic carbonates. It is also well described that the use of a co-catalyst such as Lewis acids and/or H-bond donors is very helpful to accelerate the reaction rate and/or lessen the working temperature. Hence, further supporting the overall sustainability of the target process. However, if the heterogenization of one of the cited elements is well reported in the literature, the selected heterogenized catalyst is often used with a co-catalyst in homogenous phase, discarding the possibility of an easy reuse of both partners of the reaction. There are very few examples of materials embedding both the catalyst and the co-catalyst together on the same solid.

During this thesis, multifunctional materials were designed to this very purpose and synthesized through sol-gel chemistry. Mesoporous silica materials represent an attractive support thanks to their robustness and their large surface area, ideal for heterogeneous catalysis. They also present a vast library of possible functionalization, by co- or post-synthesis. Here, both approaches were used successfully.

The various materials were all fully characterized to attest their textural and structural properties. To this end, several techniques were involved but mainly TEM, N₂ physisorption, ¹³C and ²⁹Si MAS NMR, combustion chemical analysis and ICP-OES. When applicable, a deep understanding of the insertion or functionalization of the co-catalyst was involved. The ¹¹⁹Sn NMR and Auger electron spectroscopy were involved to investigate the proper insertion of respectively the tin and zinc through co-synthesis in the silica. Thereafter, the Lewis acidity of these materials was evaluated by microcalorimetry to deeper understand the relationship between the surface of the material and the epoxide substrate. Further, the modification of the imidazolium salt to adjoin a H-bond donor was proved thanks to ¹³C MAS NMR. The interaction (often neglected) between the CO₂ and the co-activator was investigated thanks to the CO₂ adsorption coupled to IR analysis to gain an even deeper comprehension on the catalytic mechanism on the surface.

Other metals were inserted in the silica network. The titanium insertion was followed by XPS, UV-Visible spectroscopy and the importance of the post-treatment, i.e. the removal of the templating agent was demonstrated. More than its efficiency as co-catalyst with imidazolium, it showed also to be valuable for the prior step of epoxidation of alkenes to lead to a potential cascade reaction. Further, the insertion of aluminium was verified via ^{27}Al MAS NMR and the resulting acidity via microcalorimetry. To this metallic centre co-catalyst, the adjunction of two different catalysts and the synergic effect between them was questioned. The synergic effect of MgO with Al was outcompeted by the synergic effect arising from imidazolium chloride with the same Al.

Finally, it would be desirable to control more accurately the Lewis acidity on these solids. An elegant solution is provided by the organo-boron chemistry. The acidic properties of the boron-base compounds can be finely tuned by varying its substituents. In the final chapter of this thesis, a first step was achieved through the synthesis and anchoring of a pinacol borane moiety on the surface of a mesoporous silica together with an imidazolium chloride. This subject deserves a future work detailed hereafter.

Along the present work, a particular attention was dedicated to the recovering and the reusing of the materials, consistently with Green Chemistry principles. Among the 12 guidelines, some of them intrinsically match to Green Chemistry, such as the atom economy of 100 % or the use of CO_2 usually considered as a waste. The present work focusses on the comparison and understanding of the materials developed. Moreover, it worth to notice that a total conversion to cyclic carbonates can be achieved with longer reaction time or slightly increasing the amount of catalyst employed. This result together with the fact that the reaction is performed under solvent-free condition, with a total selectivity and considering that an easy separation of the catalyst via filtration or centrifugation can be easily achieved, render the entire process highly sustainable. The E factor usually calculated to evaluate the amount of waste produced compared the desired product is meaningless in this case. Moreover, the materials developed inhere bring new advantages such as the lower reaction temperature and pressure.

Hereunder, the best catalytic results employing epichlorohydrin (Table 1) or styrene oxide (Table 2) are summarized and general trends are extracted. The reaction temperature as well as the reactivity of the selected substrate are crucial to observe differences between catalysts. It is particularly clear from Entries 1-3 in Table 1. Furthermore, a positive evolution of the efficiency of the material is observed along the different chapters of this thesis. Starting from the initial bifunctional Sn-SiO₂-imi catalyst, an increased activity was observed passing to the tri-functional Sn-A-imi(II)-Cl (Table 1: Entries 3-4). The same trend as observed when styrene

oxide was employed as starting material (Table 2: Entries 1-3). It deserves to be mentioned that the importance of the nucleophile was also investigated. Enhanced performances were achieved in the series Sn-A-imi(II)-X, where X stands for Cl; Br or I (Table 2: Entries 3-6). Passing to the titanium-containing Ti-SiO₂-imi solid, a further increase of the TON was observed, overpassing the tri-functional solids for styrene oxide (Table 2: Entry 3 vs 6). Finally, the aluminium-based material demonstrated the highest activity for styrene oxide conversion (Table 2: Entry 7). In all the cases studied, an excellent selectivity was achieved (> 95 %) as well as reusability of the material. After a simple washing procedure, the conversion of the material remains the same for several cycles. This is very encouraging for future applications of these materials for the production of cyclic carbonates at larger scale.

Table 1: Catalytic conversion of epichlorohydrin using various catalysts

Entry	Catalyst	Temperature (°C)	Conv. (%)	Sel. (%)	TON
1	Sn-SiO ₂ -imi	125	53	> 95	233
2	Sn-SiO ₂ -imi	100	40	> 95	185
3	Sn-SiO ₂ -imi	80	16	> 95	78
4	Sn-A-imi(II)-Cl	80	14	> 95	107

Table 2: Catalytic conversion of styrene oxide using various catalysts

Entry	Catalyst	Temperature (°C)	Conv. (%)	Sel. (%)	TON
1	Sn-SiO ₂ -imi	125	32	> 95	96
2	Zn-SiO ₂ -imi	125	32	> 95	98
3	Sn-A-imi(II)-Cl	125	22	> 95	108
4	Sn-A-imi(II)-Br	125	36	> 95	214
5	Sn-A-imi(II)-I	125	69	> 95	449
6	Ti-SiO ₂ -E-imi	125	42	> 95	127
7	Imi/5Al_SBA-15	125	18	> 95	170

Future work

In the latest chapter of this thesis, a first approach was performed with the grafting of pinacolborane jointly with imidazolium chloride. The accomplished work is only a first step in a more complex work. A series of linker to the surface are currently under investigation to adjust the interaction with the silica surface and improve, hopefully, the stability. Then, the synthesis of new borane moieties with different substituents are envisaged to master the acidity. Along the present thesis, the general pathway was the integration by co-synthesis of the co-catalyst and followed by the grafting on the surface of the imidazolium moieties. An opposite method has been started with the successful synthesis of a periodic mesoporous silica network (PMO) embedding imidazolium by a co-synthesis approach. The co-catalyst, for instance the organoboron previously developed, could be anchored on the PMO surface afterward.

Along the present work, it has been attempted to study more deeply the interaction of the co-catalysts with the CO₂ and the epoxides substrates. This was performed using microcalorimetry and adsorption of CO₂ coupled with FT-IR. These techniques are based on the adsorption of common gas. It is very complicated to extend this study to epoxides mostly liquid at room temperature. This implementation of probe molecules to NMR could lead to even deeper understanding of the catalysis. These are very exciting challenges toward a better comprehension of the interaction of both substrates: the CO₂ and the epoxide.

A great challenge would be to get the reaction out of the lab and find application directly with flue gas instead of pure carbon dioxide. This evolution could be accompanied by the application of the catalysts to the flow chemistry. Experiments here were performed under batch condition with a stirrer, under pressure of CO₂. Several researchers demonstrated the applicability of their catalyst to the flow chemistry with the heterogeneous catalyst trapped in cartridges. Furthermore, it might be the most promising way for a operational cascade reaction starting from the alkenes.

General experimental section

Materials and Methods

N₂ physisorption

Nitrogen adsorption-desorption analyses were carried out at liquid nitrogen temperature with a volumetric adsorption analyser (Micromeritics ASAP2420 or Tristar). Prior to the analysis, the samples were pre-treated in two steps (90 °C for 1 h and 150 °C for 8 h) under reduced pressure (<10 mTorr). The Brunauer–Emmet–Teller (BET) method was applied in the 0.05–0.30 relative pressure range to calculate the specific surface area, while the pore size distributions were determined by BJH, HK or DFT method, using cylinder geometry, N₂ – Cylindrical Pores – Oxide surface model, 0.10 regularization and a version 2 deconvolution.

Transmission electron microscopy

Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai 10 microscope from the MORPHIM platform (Morphology & Imaging) operating at 80 kV. Samples were prepared by dispersion of a small quantity of material in absolute ethanol and deposited onto a copper grid.

X-Ray diffraction

X-Ray Diffraction analysis is performed on a PANalytical X'Pert diffractometer with a K α Copper radiation ($\lambda=1.54178$ Å). Analysis are performed at low-angle to assess the long-range order of the mesopores of the materials.

Inductively coupled plasma optical emission spectroscopy

Inductively coupled plasma optical emission spectroscopy (ICP-OES) employed to determine the chemical composition of the materials was performed an Optima 8000 ICP-OES Spectrometer. Digestion was performed weighting 10 mg of the solid and digesting it with aqua regia (100 μ L) and hydrofluoric acid (600 μ L) in 10.0 mL milli-Q water. Sn, Zn, Ti, B (1000 mg/L) standard solution, nitric, hydrochloric and hydrofluoric acids Ultra-quality for calibration and digestion steps were purchased from Carl Roth GmbH.

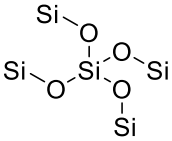
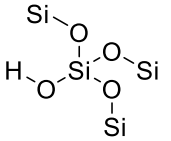
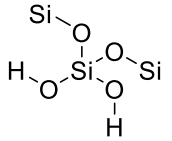
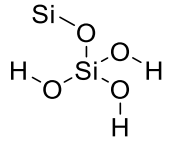
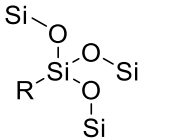
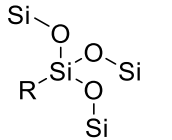
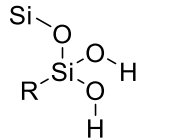
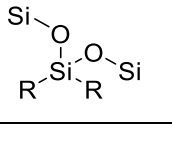
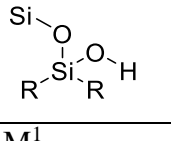
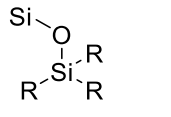
Combustion chemical analysis

Combustion chemical analyses were performed on a Perkin-Elmer 2400 Serie 2 analyser. The standard is acetanilide. This instrument was mainly used for the determination of the imidazolium content through the nitrogen amount in the material. In chapter III, the instrument allowed to confirm the complete removal of the surfactant through the carbon content.

Solid-state nuclear magnetic resonance

^{29}Si and ^{13}C NMR spectra were recorded on a Bruker Avance-500 spectrometer operating at 11.7T (99.3 MHz for ^{29}Si and 125.7 MHz for ^{13}C) using a 4 mm CP-MAS Bruker probe. The sample were packed in a zirconia rotor and measured with spinning frequencies of 8000 Hz. Cross polarization CP-MAS spectra were recorded using a 5 s relaxation delay and 5 ms contact time for ^{29}Si and 2 ms for ^{13}C . The processing comprised exponential multiplication of the FID with a line broadening factor of 30 Hz for ^{29}Si or 10 Hz for ^{13}C , zerofilling, Fourier transform, phase and baseline corrections. The chemical shift scale was calibrated at room temperature with respect to a sample of solid 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) (0.0 ppm) purchased from Sigma-Aldrich.

The classification of the ^{29}Si is summarized in the Table hereunder.

Table 1: Classification of ^{29}Si NMR signals			
Q^4 	Q^3 	Q^2 	Q^1 
	T^3 	T^2 	T^1 
		D^2 	D^1 
			M^1 

^{119}Sn NMR spectra were recorded at room temperature on a Varian VNMRS-400 spectrometer operating at 9.4 T (149 MHz for ^{119}Sn) using a 10 mm wideline probe. The sample was packed in a 10 mm Kel-F container and studied in static condition. ^{119}Sn spectra were recorded using the Hahn echo pulse sequence and following acquisition parameters: 60 s relaxation delay, 3.0 μs (90°) excitation pulse, 5 ms acquisition time. The processing comprised exponential multiplication of the FID with a line broadening factor of 1000 Hz, zero-filling, Fourier transform, phase and baseline corrections. The chemical shift scale was calibrated at room temperature with respect to the isotropic shift of SnO_2 to -603 ppm.[287]

Catalytic tests: conversion of epoxides and CO_2

All catalytic tests were performed in a *Cambridge Design Bullfrog* batch reactor. All catalysts were dried overnight at 100 $^\circ\text{C}$ prior to catalytic test. In a typical test, the solid was weighted in a Teflon vial. The epoxide (24 mL) was added without solvent. Then, the reactor was closed, purged with a gentle flow of N_2 for 10 minutes, pressurized with CO_2 (25 bar) and heated. The

mixture was stirred at 500 rpm using PTFE-coated mechanical stirrer and heated to the desired temperature with a controlled ramp. During the test, both temperature and pressure are monitored and recorded. At the end of the reaction, the reactor was cooled down to room temperature, the pressure released and the reactor opened. The reaction mixture was submitted to centrifugation for 10 min at 4500 rpm and the supernatant was analysed by ^1H -NMR using DMSO- d_6 as solvent.

The catalysts were submitted to washing prior to reuse. After removal of the epoxide/carbonate mixture by centrifugation, the catalyst was dispersed in toluene, submitted to sonication for 15 minutes and centrifuged. The supernatant is removed. The operation is repeated with ethanol as solvent. When necessary, an additional washing with HCl/ethanol was performed.

List of abbreviation

BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
bmim	1,3-butylmethylimidazolium
Bpin	pinacolborane
CHO	cyclohexene oxide
Conv.	conversion
CP	cross-polarization
CTAB	cetyltrimethylammonium bromide
DFT	density functional theory
DMSO-d6	hexadeuterated dimethylsulfoxide
DR UV-Vis	diffuse reflectance ultraviolet-visible spectroscopy
EDX	Energy-dispersive X-ray
EtOH	ethanol
FT-IR	Fourier-transform infrared
HK	Horvath-Kawazoe
ICP-OES	inductively coupled plasma – optical emission spectroscopy
IR	infrared
MAS	magic-angle spinning
MCM	Mobil Composition of Matter
MOF	metal-organic framework
NMR	nuclear magnetic resonance
psd	pore size distribution
PTFE	polytetrafluoroethylene
Q _{diff.}	differential heat of adsorption
Sel.	selectivity
SO	styrene oxide
TBAB	tetrabutylammonium bromide
TBHP	tert-butyl hydroperoxide
TEM	transmission electron microscopy
TEOS	tetraethylorthosilicate
TOF	turnover number
TON	turnover frequency

TTIP	titanium tetraisopropoxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XS-MCM	extra-small MCM

List of achievement

Published articles

1. Bi-functional heterogeneous catalysts for carbon dioxide conversion: enhanced performances at low temperature
Comès A., Collard X., Fusaro L., Atzori L., Cutrufello M.G., Aprile C.
RSC Advances, 8, pp. 25342-25350 (2018)
2. Efficient Conversion of Carbon Dioxide by Imidazolium-Based Cross-Linked Nanostructures Containing Polyhedral Oligomeric Silsesquioxane (POSS) Building Blocks
Calabrese C., Fusaro L., Liotta L.F., Giacalone F., Comès A., Campisciano V., Aprile C., Gruttadauria M.
ChemPlusChem, 84, pp. 1536-1543 (2019)
3. Multifunctional heterogeneous catalysts highly performing in the conversion of carbon dioxide: Mechanistic insights
Comès A., Fiorilli S., Aprile C.
Journal of CO₂ Utilization, 37, pp. 213-221 (2020)
4. Imidazolium-based titanosilicate nanospheres as active catalysts in carbon dioxide conversion: towards a cascade reaction from alkenes to cyclic carbonates
Comès A., Poncelet R., Pescarmona P.P., Aprile C.
Journal of CO₂ Utilization, 48 (2021) doi: 10.1016/j.jcou.2021.101529

Submitted articles

1. Supported Polyimidazolium Network on Carbon Nanoforms for the Conversion of CO₂ to Cyclic Carbonates
Morena A., Campisciano V., Comès A., Liotta L. F., Aprile C., Giacalone F., Gruttadauria M.
Submitted to Journal of CO₂ Utilization

Articles under preparation

1. Imidazolium chloride vs magnesium oxide supported on Al₂O₃/SBA-15 as catalysts for the CO₂ conversion to cyclic carbonates: on the synergistic activation mechanism
Atzori L., Comès A., Fusaro L., Aprile C., Cutrufello M.G.

2. Palladium immobilization on imidazolium based cross-linked polymers as catalysts for C-C coupling

Valentini F., Comès A., Aprile C., Vaccaro L.

Master Thesis Supervision

1. Novel method for the synthesis of size-controlled M-MCM-41 nanoparticles for the catalytic conversion of dihydroxyacetone to ethyl lactate
Nicolas Godard (2016)
2. Synthèse de matériaux mésoporeux bi-fonctionnalisés comme catalyseur pour la conversion du CO₂
Nicolas Herman (2018)
3. Synthèse de matériaux mésoporeux bi-fonctionnels pour des applications catalytiques
Rémy Poncelet (2019)
4. Effect of the support on the catalytic activity of a network of cross-linked polyvinylimidazole
Anthony Morena (2019) from the Università degli Studi di Palermo (Italy)
5. Imidazolium Salt and Boron Lewis Acids Supported on Silica as Heterogeneous Bi-functional Catalysts for the Conversion of Carbon Dioxide into Cyclic Carbonate
Sandrine Dallemagne (2021)
6. Under preparation
Jennifer Theissen (2022)

Oral Communications

1. Synthesis of bifunctional porous solids as catalysts for the conversion of carbon dioxide
Adrien Comès, Luca Fusaro, Carmela Aprile
Oral presentation at the 19th International Sol-Gel Conference 2017, in Liège (Belgium), 03rd-08th September 2017
2. Multifunctional heterogeneous catalysts highly performing in the conversion of carbon dioxide: Mechanistic insights
Adrien Comès, Sonia Fiorilli, Carmela Aprile
Oral presentation at the 13th SRC Young chemist organized by the *Société Royale de Chimie* in Namur (Belgium), 06th March 2020

Poster Communications

1. Synthesis of bifunctional porous solids as catalysts for the conversion of carbon dioxide

Adrien Comès, Luca Fusaro, Carmela Aprile

Poster presentation at the 13th European Congress on Catalysis Europacat, in Florence (Italy), 27th-31st August 2017

2. Tri-functional heterogeneous catalysts for the efficient conversion of carbon dioxide

Adrien Comès, Carmela Aprile

Poster presentation at the NISM day 2018, in Namur (Belgium), 21st September 2018

3. Synthesis of multi-functional materials as catalysts for carbon dioxide conversion

Adrien Comès, Sonia Fiorilli, Carmela Aprile

Poster presentation at the 14th European Congress on Catalysis Europacat, in Aachen (Germany), 18th-23rd August 2019

4. Synthesis of Ti-SiO₂ based catalysts for cascade reactions

Adrien Comès, Rémy Poncelet, Carmela Aprile

Poster and flash presentation at the NISM day 2019, in Namur (Belgium), 20th September 2019

References

- [1] W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, *Journal of Colloid and Interface Science*, 26 (1968) 62-69.
- [2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, *Nature*, 359 (1992) 710-712.
- [3] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, A new family of mesoporous molecular sieves prepared with liquid crystal templates, *Journal of the American Chemical Society*, 114 (1992) 10834-10843.
- [4] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, *Science*, 279 (1998) 548-552.
- [5] Q. Huo, D.I. Margolese, U. Ciesla, P. Feng, T.E. Gier, P. Sieger, R. Leon, P.M. Petroff, F. Schüth, G.D. Stucky, Generalized synthesis of periodic surfactant/inorganic composite materials, *Nature*, 368 (1994) 317-321.
- [6] J.E. Huheey, R.L. Keiter, E.A. Keiter, *Inorganic chemistry : principles of structure and reactivity*, 4th ed. 1993.
- [7] S. Che, A.E. Garcia-Bennett, T. Yokoi, K. Sakamoto, H. Kunieda, O. Terasaki, T. Tatsumi, A novel anionic surfactant templating route for synthesizing mesoporous silica with unique structure, *Nat Mater*, 2 (2003) 801-805.
- [8] L. Han, S. Che, Anionic surfactant templated mesoporous silicas (AMSS), *Chem Soc Rev*, 42 (2013) 3740-3752.
- [9] Q. Huo, D.I. Margolese, U. Ciesla, D.G. Demuth, P. Feng, T.E. Gier, P. Sieger, A. Firouzi, B.F. Chmelka, Organization of Organic Molecules with Inorganic Molecular Species into Nanocomposite Biphasic Arrays, *Chemistry of Materials*, 6 (1994) 1176-1191.
- [10] S. El Hankari, B. Motos-Perez, P. Hesemann, A. Bouhaouss, J.J. Moreau, Periodic mesoporous organosilica from zwitterionic precursors, *Chem Commun (Camb)*, 47 (2011) 6704-6706.
- [11] T. Yokoi, H. Yoshitake, T. Tatsumi, Synthesis of Anionic-Surfactant-Templated Mesoporous Silica Using Organoalkoxysilane-Containing Amino Groups, *Chemistry of Materials*, 15 (2003) 4536-4538.
- [12] P. Hesemann, T.P. Nguyen, S.E. Hankari, Precursor Mediated Synthesis of Nanostructured Silicas: From Precursor-Surfactant Ion Pairs to Structured Materials, *Materials (Basel)*, 7 (2014) 2978-3001.
- [13] R. Ryoo, C.H. Ko, M. Kruk, V. Antochshuk, M. Jaroniec, Block-Copolymer-Templated Ordered Mesoporous Silica: Array of Uniform Mesopores or Mesopore-Micropore Network?, *The Journal of Physical Chemistry B*, 104 (2000) 11465-11471.
- [14] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, Synthesis of New, Nanoporous Carbon with Hexagonally Ordered Mesopore Structure, *Journal of the American Chemical Society*, 122 (2000) 10712-10713.
- [15] M. Kruk, Access to ultralarge-pore ordered mesoporous materials through selection of surfactant/swelling-agent micellar templates, *Acc Chem Res*, 45 (2012) 1678-1687.
- [16] L. Li, X. Collard, A. Bertrand, B.F. Sels, P.P. Pescarmona, C. Aprile, Extra-small porous Sn-silicate nanoparticles as catalysts for the synthesis of lactates, *Journal of Catalysis*, 314 (2014) 56-65.
- [17] X. Collard, P. Louette, S. Fiorilli, C. Aprile, High surface area zincosilicates as efficient catalysts for the synthesis of ethyl lactate: an in-depth structural investigation, *Physical chemistry chemical physics : PCCP*, 17 (2015) 26756-26765.
- [18] X. Collard, L. Li, W. Lueangchaichaweng, A. Bertrand, C. Aprile, P.P. Pescarmona, Ga-MCM-41 nanoparticles: Synthesis and application of versatile heterogeneous catalysts, *Catalysis Today*, 235 (2014) 184-192.
- [19] N. Godard, X. Collard, A. Vivian, L.A. Bivona, S. Fiorilli, L. Fusaro, C. Aprile, Rapid room temperature synthesis of tin-based mesoporous solids: Influence of the particle size on the production of ethyl lactate, *Applied Catalysis A: General*, 556 (2018) 73-80.

- [20] X. Collard, A. Comès, C. Aprile, Mesoporous metal oxide/silica composites with photocatalytic activity and magnetic response, *Catalysis Today*, 241 (2015) 33-39.
- [21] T. Clark, J.D. Ruiz, H. Fan, C.J. Brinker, B.I. Swanson, A.N. Parikh, A New Application of UV–Ozone Treatment in the Preparation of Substrate-Supported, Mesoporous Thin Films, *Chemistry of Materials*, 12 (2000) 3879-3884.
- [22] M. Alvaro, C. Aprile, M. Benitez, E. Carbonell, H. Garcia, Photocatalytic activity of structured mesoporous TiO₂ materials, *J Phys Chem B*, 110 (2006) 6661-6665.
- [23] B. Karimi, A. Bigdeli, A.A. Safari, M. Khorasani, H. Vali, S. Khodadadi Karimvand, Aerobic Oxidation of Alcohols Catalyzed by in Situ Generated Gold Nanoparticles inside the Channels of Periodic Mesoporous Organosilica with Ionic Liquid Framework, *ACS Comb Sci*, 22 (2020) 70-79.
- [24] B. Karimi, D. Elhamifar, J.H. Clark, A.J. Hunt, Ordered mesoporous organosilica with ionic-liquid framework: an efficient and reusable support for the palladium-catalyzed Suzuki-Miyaura coupling reaction in water, *Chemistry*, 16 (2010) 8047-8053.
- [25] A. Vivian, L. Fusaro, D.P. Debecker, C. Aprile, Mesoporous Methyl-Functionalized Sn-Silicates Generated by the Aerosol Process for the Sustainable Production of Ethyl Lactate, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 14095-14103.
- [26] K. Lin, P.P. Pescarmona, K. Houthoofd, D. Liang, G. Van Tendeloo, P.A. Jacobs, Direct room-temperature synthesis of methyl-functionalized Ti-MCM-41 nanoparticles and their catalytic performance in epoxidation, *Journal of Catalysis*, 263 (2009) 75-82.
- [27] L.E. Manangon-Perugachi, A. Vivian, P. Eloy, D.P. Debecker, C. Aprile, E.M. Gaigneaux, Hydrophobic titania-silica mixed oxides for the catalytic epoxidation of cyclooctene, *Catalysis Today*, (2019).
- [28] A. Vivian, Porous structured materials embedding tin and gallium as single-site for catalytic applications: effect of the hydrophobic/hydrophilic balance, *Département de Chimie, Faculté des Sciences, Université de Namur, Namur*, 2020, pp. 172.
- [29] I. Moncayo-Riascos, B.A. Hoyos, Fluorocarbon versus hydrocarbon organosilicon surfactants for wettability alteration: A molecular dynamics approach, *Journal of Industrial and Engineering Chemistry*, 88 (2020) 224-232.
- [30] A.P. Dral, J.E. ten Elshof, Organic groups influencing microporosity in organosilicas, *Microporous and Mesoporous Materials*, 267 (2018) 267-273.
- [31] E. De Canck, Versatile Hybrid Nanomaterials: Periodic Mesoporous Organosilicas as adsorbent and catalyst, *Department of Inorganic and Physical Chemistry, Ghent University, Ghent*, 2013, pp. 245.
- [32] M. Mandal, M. Kruk, Family of Single-Micelle-Templated Organosilica Hollow Nanospheres and Nanotubes Synthesized through Adjustment of Organosilica/Surfactant Ratio, *Chemistry of Materials*, 24 (2011) 123-132.
- [33] K.J. Balkus, T.J. Pisklak, G. Hundt, J. Sibert, Y. Zhang, Photoluminescent and redox active periodic mesoporous organosilicas based on 2,7-diazapyrene, *Microporous and Mesoporous Materials*, 112 (2008) 1-13.
- [34] S.S. Park, M.S. Moorthy, C.-S. Ha, Periodic mesoporous organosilica (PMO) for catalytic applications, *Korean Journal of Chemical Engineering*, 31 (2014) 1707-1719.
- [35] T.P. Nguyen, P. Hesemann, J.J.E. Moreau, i-Silica: Nanostructured silica hybrid materials containing imidazolium groups by hydrolysis-polycondensation of disilylated bis-N,N'-alkyl-imidazolium halides, *Microporous and Mesoporous Materials*, 142 (2011) 292-300.
- [36] X. Zheng, M. Wang, Z. Sun, C. Chen, J. Ma, J. Xu, Preparation of copper (II) ion-containing bisimidazolium ionic liquid bridged periodic mesoporous organosilica and the catalytic decomposition of cyclohexyl hydroperoxide, *Catalysis Communications*, 29 (2012) 149-152.
- [37] C. Baleizão, Periodic mesoporous organosilica incorporating a catalytically active vanadyl Schiff base complex in the framework, *Journal of Catalysis*, 223 (2004) 106-113.
- [38] T. Yokoi, H. Yoshitake, T. Yamada, Y. Kubota, T. Tatsumi, Amino-functionalized mesoporous silica synthesized by an anionic surfactant templating route, *Journal of Materials Chemistry*, 16 (2006).

- [39] F. Berube, A. Khadraoui, J. Florek, S. Kaliaguine, F. Kleitz, A generalized method toward high dispersion of transition metals in large pore mesoporous metal oxide/silica hybrids, *J Colloid Interface Sci*, 449 (2015) 102-114.
- [40] F. Bérubé, B. Nohair, F. Kleitz, S. Kaliaguine, Controlled Postgrafting of Titanium Chelates for Improved Synthesis of Ti-SBA-15 Epoxidation Catalysts, *Chemistry of Materials*, 22 (2010) 1988-2000.
- [41] I. del Hierro, Y. Pérez, M. Fajardo, Heterogenization of titanium(IV) complexes with amine bis(phenolate) ligands onto SBA-15: exploring their catalytic epoxidation and electrochemical behaviour, *Applied Organometallic Chemistry*, 30 (2016) 208-214.
- [42] W. Xu, T. Ollevier, F. Kleitz, Iron-Modified Mesoporous Silica as an Efficient Solid Lewis Acid Catalyst for the Mukaiyama Aldol Reaction, *ACS Catalysis*, 8 (2018) 1932-1944.
- [43] H. Hussein, A. Vivian, L. Fusaro, M. Devillers, C. Aprile, Synthesis of Highly Accessible Gallosilicates via Impregnation Procedure: Enhanced Catalytic Performances in the Conversion of Glycerol into Solketal, *ChemCatChem*, 12 (2020) 5966-5976.
- [44] V. Smeets, L. Ben Mustapha, J. Schnee, E.M. Gaigneaux, D.P. Debecker, Mesoporous SiO₂-TiO₂ epoxidation catalysts: Tuning surface polarity to improve performance in the presence of water, *Molecular Catalysis*, 452 (2018) 123-128.
- [45] A. Vivian, L. Soumoy, L. Fusaro, S.L. Fiorilli, D.P. Debecker, C. Aprile, Surface-functionalized mesoporous gallosilicate catalysts for the efficient and sustainable upgrading of glycerol to solketal, *Green Chemistry*, (2020).
- [46] C. Aprile, F. Giacalone, P. Agrigento, L.F. Liotta, J.A. Martens, P.P. Pescarmona, M. Gruttadauria, Multilayered supported ionic liquids as catalysts for chemical fixation of carbon dioxide: a high-throughput study in supercritical conditions, *ChemSusChem*, 4 (2011) 1830-1837.
- [47] P. Agrigento, S.M. Al-Amsyar, B. Sorée, M. Taherimehr, M. Gruttadauria, C. Aprile, P.P. Pescarmona, Synthesis and high-throughput testing of multilayered supported ionic liquid catalysts for the conversion of CO₂ and epoxides into cyclic carbonates, *Catal. Sci. Technol.*, 4 (2014) 1598-1607.
- [48] L.A. Bivona, F. Quertinmont, H.A. Beejapur, F. Giacalone, M. Buaki-Sogo, M. Gruttadauria, C. Aprile, Thiazolium-Based Catalysts for the Etherification of Benzylic Alcohols under Solvent-Free Conditions, *Advanced Synthesis & Catalysis*, 357 (2015) 800-810.
- [49] A. Taralp, G. Büyükbayram, Ö. Armagan, E. Yalçın, Chemically-Tailored Surfaces of Silica Gel and Alumina Examined Using Color, *Journal of Chemical Education*, 81 (2004).
- [50] M. Janeta, L. John, J. Ejfler, S. Szafert, High-yield synthesis of amido-functionalized polyoctahedral oligomeric silsesquioxanes by using acyl chlorides, *Chemistry*, 20 (2014) 15966-15974.
- [51] R.B. Merrifield, Solid Phase Peptide Synthesis. I. The Synthesis of a Tetrapeptide, *Journal of the American Chemical Society*, 85 (1963) 2149-2154.
- [52] L. Gabrielli, L. Russo, A. Poveda, J.R. Jones, F. Nicotra, J. Jimenez-Barbero, L. Cipolla, Epoxide opening versus silica condensation during sol-gel hybrid biomaterial synthesis, *Chemistry*, 19 (2013) 7856-7864.
- [53] H.J. Hoorn, P. de Joode, W.L. Driessen, J. Reedijk, Metal-binding affinity of a series of ω -amino-alkylbenzimidazoles immobilized on silica, *Reactive and Functional Polymers*, 27 (1995) 223-235.
- [54] H.J. Hoorn, P. de Joode, W.L. Driessen, J. Reedijk, Metal-binding affinity of a series of bis(2-pyridylalkyl)amines immobilized on silica, *Recueil des Travaux Chimiques des Pays-Bas*, 115 (1996) 191-197.
- [55] H.J. Hoorn, P. de Joode, D.J. Dijkstra, W.L. Driessen, H. Kooijman, N. Veldman, A.L. Spek, J. Reedijk, Metal-binding affinity of a series of bis-benzimidazoles immobilised on silica, *Journal of Materials Chemistry*, 7 (1997) 1747-1754.
- [56] A. Ponchel, S. Abramson, J. Quartararo, D. Bormann, Y. Barbaux, E. Monflier, Cyclodextrin silica-based materials: advanced characterizations and study of their complexing behavior by diffuse reflectance UV-Vis spectroscopy, *Microporous and Mesoporous Materials*, 75 (2004) 261-272.
- [57] Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, Geneva, Switzerland, 2014, pp. 151.

- [58] P. Agrigento, F. Albericio, S. Chamoin, I. Dacquignies, H. Koc, M. Eberle, Facile and mild synthesis of linear and cyclic peptides via thioesters, *Organic letters*, 16 (2014) 3922-3925.
- [59] Mauna Loa trends in atmospheric carbon dioxide, National Oceanic and Atmospheric Administration / Earth System Research Laboratory.
- [60] E. Nisbet, Earth monitoring: Cinderella science, *Nature*, 450 (2007) 789-790.
- [61] A.P. Ballantyne, C.B. Alden, J.B. Miller, P.P. Tans, J.W. White, Increase in observed net carbon dioxide uptake by land and oceans during the past 50 years, *Nature*, 488 (2012) 70-72.
- [62] IPCC special report: Methodological and technological issues in technology transfer, 2000.
- [63] J.C. Sloopweg, Using Waste as Resource to Realize a Circular Economy: Circular Use of C, N and P, *Current Opinion in Green and Sustainable Chemistry*, (2020).
- [64] F.M. Brethomé, N.J. Williams, C.A. Seipp, M.K. Kidder, R. Custelcean, Direct air capture of CO₂ via aqueous-phase absorption and crystalline-phase release using concentrated solar power, *Nature Energy*, 3 (2018) 553-559.
- [65] Carbon Dioxide Capture and Storage: Summary for Policymakers, IPCC, 2005, pp. 16.
- [66] N.R. Galina, G.L.A.F. Arce, I. Ávila, Evolution of carbon capture and storage by mineral carbonation: Data analysis and relevance of the theme, *Minerals Engineering*, 142 (2019).
- [67] P. Viebahn, J. Nitsch, M. Fishedick, A. Esken, D. Schüwer, N. Supersberger, U. Zuberbühler, O. Edenhofer, Comparison of carbon capture and storage with renewable energy technologies regarding structural, economic, and ecological aspects in Germany, *International Journal of Greenhouse Gas Control*, 1 (2007) 121-133.
- [68] P. Styring, E.A. Quadrelli, K. Armstrong, Preface, in: P. Styring, E.A. Quadrelli, K. Armstrong (Eds.) *Carbon Dioxide Utilisation*, Elsevier, Amsterdam, 2015, pp. xv-xxiv.
- [69] M. Aresta, A. Dibenedetto, Utilisation of CO₂ as a chemical feedstock: opportunities and challenges, *Dalton Trans*, (2007) 2975-2992.
- [70] N.A. Downie, *Industrial Gases*, 2002.
- [71] J.M. DeSimone, Practical approaches to green solvents, *Science*, 297 (2002) 799-803.
- [72] C.M. Wai, F. Hunt, M. Ji, X. Chen, Chemical Reactions in Supercritical Carbon Dioxide, *Journal of Chemical Education*, 75 (1998).
- [73] M. Appl, Ammonia, 2. Production Processes, *Ullmann's Encyclopedia of Industrial Chemistry* 2011.
- [74] Z. Liu, K. Wang, Y. Chen, T. Tan, J. Nielsen, Third-generation biorefineries as the means to produce fuels and chemicals from CO₂, *Nature Catalysis*, 3 (2020) 274-288.
- [75] M. Klemenčič, A.Z. Nielsen, Y. Sakuragi, N.U. Frigaard, H. Čelešnik, P.E. Jensen, M. Dolinar, Synthetic biology of cyanobacteria for production of biofuels and high-value products, *Microalgae-Based Biofuels and Bioproducts* 2017, pp. 305-325.
- [76] I. Deniz, M. García-Vaquero, E. Imamoglu, Trends in red biotechnology, *Microalgae-Based Biofuels and Bioproducts* 2017, pp. 429-460.
- [77] J. Dexter, P. Armshaw, C. Sheahan, J.T. Pembroke, The state of autotrophic ethanol production in Cyanobacteria, *J Appl Microbiol*, 119 (2015) 11-24.
- [78] A. Schirmer, M.A. Rude, X. Li, E. Popova, S.B. del Cardayre, Microbial biosynthesis of alkanes, *Science*, 329 (2010) 559-562.
- [79] N.E. Nozzi, J.W. Oliver, S. Atsumi, Cyanobacteria as a Platform for Biofuel Production, *Front Bioeng Biotechnol*, 1 (2013) 7.
- [80] L. Al-Haj, Y.T. Lui, R.M. Abed, M.A. Goma, S. Purton, Cyanobacteria as Chassis for Industrial Biotechnology: Progress and Prospects, *Life (Basel)*, 6 (2016).
- [81] L. Gouveia, A.C. Oliveira, R. Congestri, L. Bruno, A.T. Soares, R.S. Menezes, N.R.A. Filho, I. Tzovenis, Biodiesel from microalgae, *Microalgae-Based Biofuels and Bioproducts* 2017, pp. 235-258.
- [82] Q. Schiermeier, J. Tollefson, T. Scully, A. Witze, O. Morton, Energy alternatives: Electricity without carbon, *Nature*, 454 (2008) 816-823.
- [83] K. Li, B. Peng, T. Peng, Recent Advances in Heterogeneous Photocatalytic CO₂ Conversion to Solar Fuels, *ACS Catalysis*, 6 (2016) 7485-7527.

- [84] S.N. Habisreutinger, L. Schmidt-Mende, J.K. Stolarczyk, Photocatalytic reduction of CO₂ on TiO₂ and other semiconductors, *Angew Chem Int Ed Engl*, 52 (2013) 7372-7408.
- [85] R. de Richter, S. Caillol, Fighting global warming: The potential of photocatalysis against CO₂, CH₄, N₂O, CFCs, tropospheric O₃, BC and other major contributors to climate change, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 12 (2011) 1-19.
- [86] A. Corma, H. Garcia, Photocatalytic reduction of CO₂ for fuel production: Possibilities and challenges, *Journal of Catalysis*, 308 (2013) 168-175.
- [87] H. Rao, L.C. Schmidt, J. Bonin, M. Robert, Visible-light-driven methane formation from CO₂ with a molecular iron catalyst, *Nature*, 548 (2017) 74-77.
- [88] H. Takeda, M. Ohashi, T. Tani, O. Ishitani, S. Inagaki, Enhanced photocatalysis of rhenium(II) complex by light-harvesting periodic mesoporous organosilica, *Inorg Chem*, 49 (2010) 4554-4559.
- [89] S. Ma, M. Sadakiyo, M. Heima, R. Luo, R.T. Haasch, J.I. Gold, M. Yamauchi, P.J. Kenis, Electroreduction of Carbon Dioxide to Hydrocarbons Using Bimetallic Cu-Pd Catalysts with Different Mixing Patterns, *J Am Chem Soc*, 139 (2017) 47-50.
- [90] J. Wang, Z. Li, C. Dong, Y. Feng, J. Yang, H. Liu, X. Du, Silver/Copper Interface for Relay Electroreduction of Carbon Dioxide to Ethylene, *ACS Appl Mater Interfaces*, 11 (2019) 2763-2767.
- [91] S. Back, J.H. Kim, Y.T. Kim, Y. Jung, Bifunctional Interface of Au and Cu for Improved CO₂ Electroreduction, *ACS Appl Mater Interfaces*, 8 (2016) 23022-23027.
- [92] Y. Wu, Z. Jiang, X. Lu, Y. Liang, H. Wang, Domino electroreduction of CO₂ to methanol on a molecular catalyst, *Nature*, 575 (2019) 639-642.
- [93] Y. Song, R. Peng, D.K. Hensley, P.V. Bonnesen, L. Liang, Z. Wu, H.M. Meyer, M. Chi, C. Ma, B.G. Sumpter, A.J. Rondinone, High-Selectivity Electrochemical Conversion of CO₂ to Ethanol using a Copper Nanoparticle/N-Doped Graphene Electrode, *ChemistrySelect*, 1 (2016) 6055-6061.
- [94] Y. Wang, Z. Wang, C.-T. Dinh, J. Li, A. Ozden, M. Golam Kibria, A. Seifitokaldani, C.-S. Tan, C.M. Gabardo, M. Luo, H. Zhou, F. Li, Y. Lum, C. McCallum, Y. Xu, M. Liu, A. Proppe, A. Johnston, P. Todorovic, T.-T. Zhuang, D. Sinton, S.O. Kelley, E.H. Sargent, Catalyst synthesis under CO₂ electroreduction favours faceting and promotes renewable fuels electrosynthesis, *Nature Catalysis*, 3 (2019) 98-106.
- [95] D.T. Whipple, P.J.A. Kenis, Prospects of CO₂ Utilization via Direct Heterogeneous Electrochemical Reduction, *The Journal of Physical Chemistry Letters*, 1 (2010) 3451-3458.
- [96] F. Li, Y.C. Li, Z. Wang, J. Li, D.-H. Nam, Y. Lum, M. Luo, X. Wang, A. Ozden, S.-F. Hung, B. Chen, Y. Wang, J. Wicks, Y. Xu, Y. Li, C.M. Gabardo, C.-T. Dinh, Y. Wang, T.-T. Zhuang, D. Sinton, E.H. Sargent, Cooperative CO₂-to-ethanol conversion via enriched intermediates at molecule-metal catalyst interfaces, *Nature Catalysis*, 3 (2019) 75-82.
- [97] B.M. Tackett, E. Gomez, J.G. Chen, Net reduction of CO₂ via its thermocatalytic and electrocatalytic transformation reactions in standard and hybrid processes, *Nature Catalysis*, 2 (2019) 381-386.
- [98] J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun, Directly converting CO₂ into a gasoline fuel, *Nat Commun*, 8 (2017) 15174.
- [99] P. Gao, S. Li, X. Bu, S. Dang, Z. Liu, H. Wang, L. Zhong, M. Qiu, C. Yang, J. Cai, W. Wei, Y. Sun, Direct conversion of CO₂ into liquid fuels with high selectivity over a bifunctional catalyst, *Nat Chem*, 9 (2017) 1019-1024.
- [100] Y. Wang, S. Kazumi, W. Gao, X. Gao, H. Li, X. Guo, Y. Yoneyama, G. Yang, N. Tsubaki, Direct conversion of CO₂ to aromatics with high yield via a modified Fischer-Tropsch synthesis pathway, *Applied Catalysis B: Environmental*, 269 (2020).
- [101] D.S. Marlin, E. Sarron, O. Sigurbjornsson, Process Advantages of Direct CO₂ to Methanol Synthesis, *Front Chem*, 6 (2018) 446.
- [102] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre, P. Prabhakaran, S. Bajohr, Review on methanation – From fundamentals to current projects, *Fuel*, 166 (2016) 276-296.
- [103] R. Gaikwad, H. Reymond, N. Phongprueksathat, P. Rudolf von Rohr, A. Urakawa, From CO or CO₂?: space-resolved insights into high-pressure CO₂ hydrogenation to methanol over Cu/ZnO/Al₂O₃, *Catalysis Science & Technology*, 10 (2020) 2763-2768.

- [104] X. Nie, W. Li, X. Jiang, X. Guo, C. Song, Recent advances in catalytic CO₂ hydrogenation to alcohols and hydrocarbons, 2019, pp. 121-233.
- [105] I. Dincer, C. Acar, Innovation in hydrogen production, *International Journal of Hydrogen Energy*, 42 (2017) 14843-14864.
- [106] S.A. Al-Saydeh, S.J. Zaidi, Carbon Dioxide Conversion to Methanol: Opportunities and Fundamental Challenges, *Carbon Dioxide Chemistry, Capture and Oil Recovery* 2018.
- [107] M. North, Across the Board: Michael North on Carbon Dioxide Biorefinery, *ChemSusChem*, 12 (2019) 1763-1765.
- [108] Q. Liu, L. Wu, R. Jackstell, M. Beller, Using carbon dioxide as a building block in organic synthesis, *Nat Commun*, 6 (2015) 5933.
- [109] C. Nitschke, G. Scherr, Urea Derivatives, *Ullmann's Encyclopedia of Industrial Chemistry* 2010.
- [110] F. Mani, M. Peruzzini, P. Stoppioni, CO₂ absorption by aqueous NH₃ solutions: speciation of ammonium carbamate, bicarbonate and carbonate by a ¹³C NMR study, *Green Chemistry*, 8 (2006).
- [111] A.W. Kleij, M. North, A. Urakawa, CO₂ Catalysis, *ChemSusChem*, 10 (2017) 1036-1038.
- [112] L. Guo, K.J. Lamb, M. North, Recent developments in organocatalysed transformations of epoxides and carbon dioxide into cyclic carbonates, *Green Chemistry*, (2021).
- [113] B. Grignard, S. Gennen, C. Jerome, A.W. Kleij, C. Detrembleur, Advances in the use of CO₂ as a renewable feedstock for the synthesis of polymers, *Chem Soc Rev*, 48 (2019) 4466-4514.
- [114] F. Mizuno, S. Nakanishi, Y. Kotani, S. Yokoishi, H. Iba, Rechargeable Li-Air Batteries with Carbonate-Based Liquid Electrolytes, *Electrochemistry*, 78 (2010) 403-405.
- [115] X. Li, M. Banis, A. Lushington, X. Yang, Q. Sun, Y. Zhao, C. Liu, Q. Li, B. Wang, W. Xiao, C. Wang, M. Li, J. Liang, R. Li, Y. Hu, L. Goncharova, H. Zhang, T.K. Sham, X. Sun, A high-energy sulfur cathode in carbonate electrolyte by eliminating polysulfides via solid-phase lithium-sulfur transformation, *Nat Commun*, 9 (2018) 4509.
- [116] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, A novel non-phosgene polycarbonate production process using by-product CO₂ as starting material, *Green Chem.*, 5 (2003) 497-507.
- [117] M. Tamura, K. Ito, M. Honda, Y. Nakagawa, H. Sugimoto, K. Tomishige, Direct Copolymerization of CO₂ and Diols, *Sci Rep*, 6 (2016) 24038.
- [118] K. Tezuka, K. Komatsu, O. Haba, The anionic ring-opening polymerization of five-membered cyclic carbonates fused to the cyclohexane ring, *Polymer Journal*, 45 (2013) 1183-1187.
- [119] M. Taherimehr, P.P. Pescarmona, Green polycarbonates prepared by the copolymerization of CO₂ with epoxides, *Journal of Applied Polymer Science*, 131 (2014) n/a-n/a.
- [120] V. Saptal, D.B. Shinde, R. Banerjee, B.M. Bhanage, State-of-the-art catechol porphyrin COF catalyst for chemical fixation of carbon dioxide via cyclic carbonates and oxazolidinones, *Catalysis Science & Technology*, 6 (2016) 6152-6158.
- [121] N. Kihara, N. Hara, T. Endo, Catalytic activity of various salts in the reaction of 2,3-epoxypropyl phenyl ether and carbon dioxide under atmospheric pressure, *The Journal of Organic Chemistry*, 58 (1993) 6198-6202.
- [122] T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda, J.Y. Hasegawa, Bifunctional porphyrin catalysts for the synthesis of cyclic carbonates from epoxides and CO₂: structural optimization and mechanistic study, *J Am Chem Soc*, 136 (2014) 15270-15279.
- [123] T. Ema, K. Fukuhara, T. Sakai, M. Ohbo, F.-Q. Bai, J.-y. Hasegawa, Quaternary ammonium hydroxide as a metal-free and halogen-free catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide, *Catalysis Science & Technology*, 5 (2015) 2314-2321.
- [124] J.A. Castro-Osma, M. North, W.K. Offermans, W. Leitner, T.E. Muller, Unprecedented Carbonato Intermediates in Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium(Salen) Complexes, *ChemSusChem*, 9 (2016) 791-794.
- [125] C. Maeda, M. Mitsuzane, T. Ema, Chiral Bifunctional Metalloporphyrin Catalysts for Kinetic Resolution of Epoxides with Carbon Dioxide, *Organic letters*, 21 (2019) 1853-1856.

- [126] G. Fiorani, W. Guo, A.W. Kleij, Sustainable conversion of carbon dioxide: the advent of organocatalysis, *Green Chemistry*, 17 (2015) 1375-1389.
- [127] F. Jutz, J.M. Andanson, A. Baiker, Ionic liquids and dense carbon dioxide: a beneficial biphasic system for catalysis, *Chem Rev*, 111 (2011) 322-353.
- [128] M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing, C. Detrembleur, Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: catalyst design and mechanistic studies, *Catalysis Science & Technology*, 7 (2017) 2651-2684.
- [129] R.G. Pearson, J. Songstad, Application of the Principle of Hard and Soft Acids and Bases to Organic Chemistry, *Journal of the American Chemical Society*, 89 (1967) 1827-1836.
- [130] J. Melendez, M. North, P. Villuendas, One-component catalysts for cyclic carbonate synthesis, *Chem Commun (Camb)*, 0 (2009) 2577-2579.
- [131] P.P. Pescarmona, M. Taherimehr, Challenges in the catalytic synthesis of cyclic and polymeric carbonates from epoxides and CO₂, *Catalysis Science & Technology*, 2 (2012) 2169-2187.
- [132] F.D. Bobbink, A.P. van Muyden, P.J. Dyson, En route to CO₂-containing renewable materials: catalytic synthesis of polycarbonates and non-isocyanate polyhydroxyurethanes derived from cyclic carbonates, *Chem Commun (Camb)*, 55 (2019) 1360-1373.
- [133] F. Ahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, A.R. Khosropour, Highly efficient chemical fixation of carbon dioxide catalyzed by high-valent tetraphenylporphyrinatotin(IV) triflate, *Inorganic Chemistry Communications*, 14 (2011) 1489-1493.
- [134] M.V. Escarcega-Bobadilla, M. Martinez Belmonte, E. Martin, E.C. Escudero-Adan, A.W. Kleij, A recyclable trinuclear bifunctional catalyst derived from a tetraoxo bis-Zn(salphen) metalloligand, *Chemistry*, 19 (2013) 2641-2648.
- [135] C. Maeda, T. Taniguchi, K. Ogawa, T. Ema, Bifunctional catalysts based on m-phenylene-bridged porphyrin dimer and trimer platforms: synthesis of cyclic carbonates from carbon dioxide and epoxides, *Angew Chem Int Ed Engl*, 54 (2015) 134-138.
- [136] T. Sakakura, J.C. Choi, H. Yasuda, Transformation of carbon dioxide, *Chem Rev*, 107 (2007) 2365-2387.
- [137] J.-Q. Wang, W.-G. Cheng, J. Sun, T.-Y. Shi, X.-P. Zhang, S.-J. Zhang, Efficient fixation of CO₂ into organic carbonates catalyzed by 2-hydroxymethyl-functionalized ionic liquids, *RSC Adv.*, 4 (2014) 2360-2367.
- [138] M.H. Anthofer, M.E. Wilhelm, M. Cokoja, M. Drees, W.A. Herrmann, F.E. Kühn, Hydroxy-Functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO₂ and Epoxides to Cyclic Carbonates, *ChemCatChem*, 7 (2015) 94-98.
- [139] Y. Li, B. Dominelli, R.M. Reich, B. Liu, F.E. Kühn, Bridge-functionalized bisimidazolium bromides as catalysts for the conversion of epoxides to cyclic carbonates with CO₂, *Catalysis Communications*, 124 (2019) 118-122.
- [140] M. Aresta, A. Dibenedetto, E. Quaranta, CO₂ Coordination to Metal Centres: Modes of Bonding and Reactivity, *Reaction Mechanisms in Carbon Dioxide Conversion*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2016, pp. 35-69.
- [141] X.-J. Hou, P. He, H. Li, X. Wang, Understanding the Adsorption Mechanism of C₂H₂, CO₂, and CH₄ in Isostructural Metal–Organic Frameworks with Coordinatively Unsaturated Metal Sites, *The Journal of Physical Chemistry C*, 117 (2013) 2824-2834.
- [142] L.-F. Xiao, F.-W. Li, J.-J. Peng, C.-G. Xia, Immobilized ionic liquid/zinc chloride: Heterogeneous catalyst for synthesis of cyclic carbonates from carbon dioxide and epoxides, *Journal of Molecular Catalysis A: Chemical*, 253 (2006) 265-269.
- [143] L. Han, S.-W. Park, D.-W. Park, Silica grafted imidazolium-based ionic liquids: efficient heterogeneous catalysts for chemical fixation of CO₂ to a cyclic carbonate, *Energy & Environmental Science*, 2 (2009).
- [144] L. Han, M.-S. Park, S.-J. Choi, Y.-J. Kim, S.-M. Lee, D.-W. Park, Incorporation of Metal Ions into Silica-Grafted Imidazolium-Based Ionic Liquids to Efficiently Catalyze Cycloaddition Reactions of CO₂ and Epoxides, *Catalysis Letters*, 142 (2011) 259-266.

- [145] L.A. Bivona, O. Fichera, L. Fusaro, F. Giacalone, M. Buaki-Sogo, M. Gruttadauria, C. Aprile, A polyhedral oligomeric silsesquioxane-based catalyst for the efficient synthesis of cyclic carbonates, *Catalysis Science & Technology*, 5 (2015) 5000-5007.
- [146] M. Taherimehr, B. Van de Voorde, L.H. Wee, J.A. Martens, D.E. De Vos, P.P. Pescarmona, Strategies for Enhancing the Catalytic Performance of Metal-Organic Frameworks in the Fixation of CO₂ into Cyclic Carbonates, *ChemSusChem*, 10 (2017) 1283-1291.
- [147] C. Calabrese, F. Giacalone, C. Aprile, Hybrid Catalysts for CO₂ Conversion into Cyclic Carbonates, *Catalysts*, 9 (2019).
- [148] J. Liang, Y.-B. Huang, R. Cao, Metal-organic frameworks and porous organic polymers for sustainable fixation of carbon dioxide into cyclic carbonates, *Coordination Chemistry Reviews*, 378 (2019) 32-65.
- [149] W.Y. Gao, Y. Chen, Y. Niu, K. Williams, L. Cash, P.J. Perez, L. Wojtas, J. Cai, Y.S. Chen, S. Ma, Crystal engineering of an nbo topology metal-organic framework for chemical fixation of CO₂ under ambient conditions, *Angew Chem Int Ed Engl*, 53 (2014) 2615-2619.
- [150] R. Luo, X. Zhou, Y. Fang, H. Ji, Metal- and solvent-free synthesis of cyclic carbonates from epoxides and CO₂ in the presence of graphite oxide and ionic liquid under mild conditions: A kinetic study, *Carbon*, 82 (2015) 1-11.
- [151] G.L.M. Léonard, A. Belet, B. Grignard, C. Calberg, B. Gilbert, C. Jérôme, B. Heinrichs, Heterogenization of a cyclocarbonation catalyst: Optimization and kinetic study, *Catalysis Today*, 334 (2019) 140-155.
- [152] G.L.M. Léonard, S.L. Pirard, A. Belet, B. Grignard, C. Detrembleur, C. Jérôme, B. Heinrichs, Optimizing support properties of heterogeneous catalysts for the coupling of carbon dioxide with epoxides, *Chemical Engineering Journal*, 371 (2019) 719-729.
- [153] S. Baj, T. Krawczyk, K. Jasiak, A. Siewniak, M. Pawlyta, Catalytic coupling of epoxides and CO₂ to cyclic carbonates by carbon nanotube-supported quaternary ammonium salts, *Applied Catalysis A: General*, 488 (2014) 96-102.
- [154] X. Zhou, Y. Zhang, X. Yang, L. Zhao, G. Wang, Functionalized IRMOF-3 as efficient heterogeneous catalyst for the synthesis of cyclic carbonates, *Journal of Molecular Catalysis A: Chemical*, 361-362 (2012) 12-16.
- [155] D. Ma, B. Li, K. Liu, X. Zhang, W. Zou, Y. Yang, G. Li, Z. Shi, S. Feng, Bifunctional MOF heterogeneous catalysts based on the synergy of dual functional sites for efficient conversion of CO₂ under mild and co-catalyst free conditions, *Journal of Materials Chemistry A*, 3 (2015) 23136-23142.
- [156] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, Synergistic hybrid catalyst for cyclic carbonate synthesis: remarkable acceleration caused by immobilization of homogeneous catalyst on silica, *Chem Commun (Camb)*, (2006) 1664-1666.
- [157] T. Sakai, Y. Tsutsumi, T. Ema, Highly active and robust organic-inorganic hybrid catalyst for the synthesis of cyclic carbonates from carbon dioxide and epoxides, *Green Chemistry*, 10 (2008).
- [158] J. Steinbauer, L. Longwitz, M. Frank, J. Epping, U. Kragl, T. Werner, Immobilized bifunctional phosphonium salts as recyclable organocatalysts in the cycloaddition of CO₂ and epoxides, *Green Chemistry*, 19 (2017) 4435-4445.
- [159] W. Cheng, X. Chen, J. Sun, J. Wang, S. Zhang, SBA-15 supported triazolium-based ionic liquids as highly efficient and recyclable catalysts for fixation of CO₂ with epoxides, *Catalysis Today*, 200 (2013) 117-124.
- [160] L.J. Zhou, W. Sun, N.N. Yang, P. Li, T. Gong, W.J. Sun, Q. Sui, E.Q. Gao, A Facile and Versatile "Click" Approach Toward Multifunctional Ionic Metal-organic Frameworks for Efficient Conversion of CO₂, *ChemSusChem*, 12 (2019) 2202-2210.
- [161] A. Mirabaud, A. Martinez, F. Bayard, J.-P. Dutasta, V. Dufaud, A new heterogeneous host-guest catalytic system as an eco-friendly approach for the synthesis of cyclic carbonates from CO₂ and epoxides, *New Journal of Chemistry*, 42 (2018) 16863-16874.

- [162] A. Mirabaud, J.-C. Mulatier, A. Martinez, J.-P. Dutasta, V. Dufaud, Investigating Host–Guest Complexes in the Catalytic Synthesis of Cyclic Carbonates from Styrene Oxide and CO₂, *ACS Catalysis*, 5 (2015) 6748-6752.
- [163] T. Ema, Y. Miyazaki, T. Taniguchi, J. Takada, Robust porphyrin catalysts immobilized on biogenous iron oxide for the repetitive conversions of epoxides and CO₂ into cyclic carbonates, *Green Chemistry*, 15 (2013).
- [164] M. North, P. Villuendas, C. Young, A gas-phase flow reactor for ethylene carbonate synthesis from waste carbon dioxide, *Chemistry*, 15 (2009) 11454-11457.
- [165] J. Melendez, M. North, P. Villuendas, C. Young, One-component bimetallic aluminium(salen)-based catalysts for cyclic carbonate synthesis and their immobilization, *Dalton Trans*, 40 (2011) 3885-3902.
- [166] M. North, P. Villuendas, Influence of Support and Linker Parameters on the Activity of Silica-Supported Catalysts for Cyclic Carbonate Synthesis, *ChemCatChem*, 4 (2012) 789-794.
- [167] Y. Wang, J. Nie, C. Lu, F. Wang, C. Ma, Z. Chen, G. Yang, Imidazolium-based polymeric ionic liquids for heterogeneous catalytic conversion of CO₂ into cyclic carbonates, *Microporous and Mesoporous Materials*, 292 (2020).
- [168] H. Zhong, Y. Su, X. Chen, X. Li, R. Wang, Imidazolium- and Triazine-Based Porous Organic Polymers for Heterogeneous Catalytic Conversion of CO₂ into Cyclic Carbonates, *ChemSusChem*, 10 (2017) 4855-4863.
- [169] Y. Wang, X. Guan, F. Chen, S. Zhu, Y. Ye, H. Peng, X. Zhou, X. Xie, Y. Mai, Noncovalent immobilization of pyrene-terminated hyperbranched triazole-based polymeric ionic liquid onto graphene for highly active and recyclable catalysis of CO₂/epoxide cycloaddition, *Catalysis Science & Technology*, 7 (2017) 4173-4181.
- [170] A. Dani, V. Crocellà, C. Magistris, V. Santoro, J. Yuan, S. Bordiga, Click-based porous cationic polymers for enhanced carbon dioxide capture, *Journal of Materials Chemistry A*, 5 (2017) 372-383.
- [171] J. Yuan, M. Antonietti, Poly(ionic liquid)s: Polymers expanding classical property profiles, *Polymer*, 52 (2011) 1469-1482.
- [172] J. Yuan, D. Mecerreyes, M. Antonietti, Poly(ionic liquid)s: An update, *Progress in Polymer Science*, 38 (2013) 1009-1036.
- [173] M. Buaki-Sogó, A. Vivian, L.A. Bivona, H. García, M. Gruttadauria, C. Aprile, Imidazolium functionalized carbon nanotubes for the synthesis of cyclic carbonates: reducing the gap between homogeneous and heterogeneous catalysis, *Catalysis Science & Technology*, 6 (2016) 8418-8427.
- [174] C. Calabrese, L.F. Liotta, E. Carbonell, F. Giacalone, M. Gruttadauria, C. Aprile, Imidazolium-Functionalized Carbon Nanohorns for the Conversion of Carbon Dioxide: Unprecedented Increase of Catalytic Activity after Recycling, *ChemSusChem*, 10 (2017) 1202-1209.
- [175] Y. Hu, S. Peglow, L. Longwitz, M. Frank, J.D. Epping, V. Bruser, T. Werner, Plasma-Assisted Immobilization of a Phosphonium Salt and Its Use as a Catalyst in the Valorization of CO₂, *ChemSusChem*, 13 (2020) 1825-1833.
- [176] W. Wang, Y. Wang, C. Li, L. Yan, M. Jiang, Y. Ding, State-of-the-Art Multifunctional Heterogeneous POP Catalyst for Cooperative Transformation of CO₂ to Cyclic Carbonates, *ACS Sustainable Chemistry & Engineering*, 5 (2017) 4523-4528.
- [177] Y. Chen, R. Luo, Q. Ren, X. Zhou, H. Ji, Click-Based Porous Ionic Polymers with Intercalated High-Density Metalloporphyrin for Sustainable CO₂ Transformation, *Industrial & Engineering Chemistry Research*, 59 (2020) 20269-20277.
- [178] S. Jayakumar, H. Li, J. Chen, Q. Yang, Cationic Zn-Porphyrin Polymer Coated onto CNTs as a Cooperative Catalyst for the Synthesis of Cyclic Carbonates, *ACS Appl Mater Interfaces*, 10 (2018) 2546-2555.
- [179] W.-L. Dai, L. Chen, S.-F. Yin, W.-H. Li, Y.-Y. Zhang, S.-L. Luo, C.-T. Au, High-Efficiency Synthesis of Cyclic Carbonates from Epoxides and CO₂ over Hydroxyl Ionic Liquid Catalyst Grafted onto Cross-Linked Polymer, *Catalysis Letters*, 137 (2010) 74-80.

- [180] C. Calabrese, L.F. Liotta, F. Giacalone, M. Gruttadauria, C. Aprile, Supported Polyhedral Oligomeric Silsesquioxane-Based (POSS) Materials as Highly Active Organocatalysts for the Conversion of CO₂, *ChemCatChem*, 11 (2019) 560-567.
- [181] L. Feng, J. Wang, L. Chen, M. Lu, Z. Zheng, R. Jing, H. Chen, X. Shen, A Green Strategy to Enhance a Liquid-Liquid Heterogeneous Reaction with a Magnetic Recyclable Pickering Emulsion, *ChemCatChem*, 7 (2015) 616-624.
- [182] R. Luo, X. Liu, M. Chen, B. Liu, Y. Fang, Recent Advances on Imidazolium-Functionalized Organic Cationic Polymers for CO₂ Adsorption and Simultaneous Conversion into Cyclic Carbonates, *ChemSusChem*, 13 (2020) 3945-3966.
- [183] J. Liang, Y.Q. Xie, Q. Wu, X.Y. Wang, T.T. Liu, H.F. Li, Y.B. Huang, R. Cao, Zinc Porphyrin/Imidazolium Integrated Multivariate Zirconium Metal-Organic Frameworks for Transformation of CO₂ into Cyclic Carbonates, *Inorg Chem*, 57 (2018) 2584-2593.
- [184] J.F. Kurisingal, Y. Rachuri, R.S. Pillai, Y. Gu, Y. Choe, D.W. Park, Ionic-Liquid-Functionalized UiO-66 Framework: An Experimental and Theoretical Study on the Cycloaddition of CO₂ and Epoxides, *ChemSusChem*, 12 (2019) 1033-1042.
- [185] L.G. Ding, B.J. Yao, W.L. Jiang, J.T. Li, Q.J. Fu, Y.A. Li, Z.H. Liu, J.P. Ma, Y.B. Dong, Bifunctional Imidazolium-Based Ionic Liquid Decorated UiO-67 Type MOF for Selective CO₂ Adsorption and Catalytic Property for CO₂ Cycloaddition with Epoxides, *Inorg Chem*, 56 (2017) 2337-2344.
- [186] J. Liang, Y.Q. Xie, X.S. Wang, Q. Wang, T.T. Liu, Y.B. Huang, R. Cao, An imidazolium-functionalized mesoporous cationic metal-organic framework for cooperative CO₂ fixation into cyclic carbonate, *Chem Commun (Camb)*, 54 (2018) 342-345.
- [187] M. Ding, H.-L. Jiang, Incorporation of Imidazolium-Based Poly(ionic liquid)s into a Metal–Organic Framework for CO₂ Capture and Conversion, *ACS Catalysis*, (2018) 3194-3201.
- [188] P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.
- [189] M. Poliakoff, J.M. Fitzpatrick, T.R. Farren, P.T. Anastas, Green chemistry: science and politics of change, *Science*, 297 (2002) 807-810.
- [190] R.A. Sheldon, Metrics of Green Chemistry and Sustainability: Past, Present, and Future, *ACS Sustainable Chemistry & Engineering*, 6 (2017) 32-48.
- [191] T. Zhang, J. Yin, Y. Pan, E. Liu, D. Liu, J. Meng, Hierarchical porous polyimide nanocomposite membrane for flow-through CO₂ cycloaddition at mild conditions, *Chemical Engineering Journal*, 383 (2020).
- [192] N. Cardonamartinez, Acid strength of silica-alumina and silica studied by microcalorimetric measurements of pyridine adsorption, *Journal of Catalysis*, 125 (1990) 427-444.
- [193] G. Colón, I. Ferino, E. Rombi, E. Selli, L. Forni, P. Magnoux, M. Guisnet, Liquid-phase alkylation of naphthalene by isopropanol over zeolites. Part 1: HY zeolites, *Applied Catalysis A: General*, 168 (1998) 81-92.
- [194] D. Meloni, D. Perra, R. Monaci, M.G. Cutrufello, E. Rombi, I. Ferino, Transesterification of *Jatropha curcas* oil and soybean oil on Al-SBA-15 catalysts, *Applied Catalysis B: Environmental*, 184 (2016) 163-173.
- [195] N. Fattori, C.M. Maroneze, L.P. da Costa, M. Strauss, F.A. Sigoli, I.O. Mazali, Y. Gushikem, Ion-exchange properties of imidazolium-grafted SBA-15 toward AuCl₄(-) anions and their conversion into supported gold nanoparticles, *Langmuir*, 28 (2012) 10281-10288.
- [196] L. Wang, E.Y.X. Chen, Recyclable Supported Carbene Catalysts for High-Yielding Self-Condensation of Furaldehydes into C10 and C12 Furoins, *ACS Catalysis*, 5 (2015) 6907-6917.
- [197] N. Godard, A. Vivian, L. Fusaro, L. Cannavici, C. Aprile, D.P. Debecker, High-Yield Synthesis of Ethyl Lactate with Mesoporous Tin Silicate Catalysts Prepared by an Aerosol-Assisted Sol-Gel Process, *ChemCatChem*, 9 (2017) 2211-2218.
- [198] P. Shah, A.V. Ramaswamy, K. Lazar, V. Ramaswamy, Direct hydrothermal synthesis of mesoporous Sn-SBA-15 materials under weak acidic conditions, *Microporous and Mesoporous Materials*, 100 (2007) 210-226.

- [199] E.V. Beletskiy, X. Hou, Z. Shen, J.R. Gallagher, J.T. Miller, Y. Wu, T. Li, M.C. Kung, H.H. Kung, Supported Tetrahedral Oxo-Sn Catalyst: Single Site, Two Modes of Catalysis, *J Am Chem Soc*, 138 (2016) 4294-4297.
- [200] S.E. Ashbrook, S. Seddon, New methods and applications in solid-state NMR spectroscopy of quadrupolar nuclei, *J Am Chem Soc*, 136 (2014) 15440-15456.
- [201] G. Horváth, K. Kawazoe, Method for the calculation of effective pore size distribution in molecular sieve carbon, *Journal of Chemical Engineering of Japan*, 16 (1983) 470-475.
- [202] P.L. Llewellyn, E. Bloch, S. Bourrelly, Surface Area/Porosity, Adsorption, Diffusion, Characterization of Solid Materials and Heterogeneous Catalysts, Wiley-VCH Verlag GmbH & Co. KGaA2012, pp. 853-879.
- [203] M. Buaki-Sogo, H. Garcia, C. Aprile, Imidazolium-based silica microreactors for the efficient conversion of carbon dioxide, *Catalysis Science & Technology*, 5 (2015) 1222-1230.
- [204] J. Lan, M. Liu, X. Lu, X. Zhang, J. Sun, Novel 3D Nitrogen-Rich Metal Organic Framework for Highly Efficient CO₂ Adsorption and Catalytic Conversion to Cyclic Carbonates under Ambient Temperature, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 8727-8735.
- [205] X. Guo, Z. Zhou, C. Chen, J. Bai, C. He, C. Duan, New rht-Type Metal-Organic Frameworks Decorated with Acylamide Groups for Efficient Carbon Dioxide Capture and Chemical Fixation from Raw Power Plant Flue Gas, *ACS Appl Mater Interfaces*, 8 (2016) 31746-31756.
- [206] Z. Xue, J. Jiang, M.-G. Ma, M.-F. Li, T. Mu, Gadolinium-Based Metal–Organic Framework as an Efficient and Heterogeneous Catalyst To Activate Epoxides for Cycloaddition of CO₂ and Alcoholysis, *ACS Sustainable Chemistry & Engineering*, 5 (2017) 2623-2631.
- [207] J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang, B. Han, MOF-5/n-Bu₄NBr: an efficient catalyst system for the synthesis of cyclic carbonates from epoxides and CO₂ under mild conditions, *Green Chemistry*, 11 (2009) 1031-1036.
- [208] Y. Ren, Y. Shi, J. Chen, S. Yang, C. Qi, H. Jiang, Ni(salphen)-based metal–organic framework for the synthesis of cyclic carbonates by cycloaddition of CO₂ to epoxides, *RSC Advances*, 3 (2013) 2167-2170.
- [209] D. Srinivas, P. Ratnasamy, Spectroscopic and catalytic properties of SBA-15 molecular sieves functionalized with acidic and basic moieties, *Microporous and Mesoporous Materials*, 105 (2007) 170-180.
- [210] A. Comès, X. Collard, L. Fusaro, L. Atzori, M.G. Cutrufello, C. Aprile, Bi-functional heterogeneous catalysts for carbon dioxide conversion: enhanced performances at low temperature, *RSC Advances*, 8 (2018) 25342-25350.
- [211] K. Ebel, H. Koehler, A.O. Gamer, R. Jäckh, Imidazole and Derivatives, *Ullmann's Encyclopedia of Industrial Chemistry*2000.
- [212] J.-P. Lindner, Imidazolium-Based Polymers via the Poly-Radziszewski Reaction, *Macromolecules*, 49 (2016) 2046-2053.
- [213] R. Martínez, R. Torregrosa, I.M. Pastor, M. Yus, Isoprene as Lithiation Mediator: Synthesis of 2-Substituted 1-Alkylimidazole Derivatives, *Synthesis*, 44 (2012) 2630-2638.
- [214] J.D. Holbrey, M.B. Turner, W.M. Reichert, R.D. Rogers, New ionic liquids containing an appended hydroxyl functionality from the atom-efficient, one-pot reaction of 1-methylimidazole and acid with propylene oxide, *Green Chemistry*, 5 (2003) 731-736.
- [215] A. Ueno, C.O. Bennett, Infrared study of CO₂ adsorption on SiO₂, *Journal of Catalysis*, 54 (1978) 31-41.
- [216] H. Knoezinger, E. Taglauer, Toward supported oxide catalysts via solid-solid wetting, *Catalysis*, 10 (1993) 1-40.
- [217] C.O. Areán, M.R. Delgado, Variable-temperature FT-IR studies on the thermodynamics of carbon dioxide adsorption on a faujasite-type H-Y zeolite, *Applied Surface Science*, 256 (2010) 5259-5262.
- [218] P.A. Webb, O. Clyde, *Analytical Methods in Fine Particle Technology*, Micromeritics Instrument Corporation, Norcross (U.S.A.), 1997.

- [219] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure and Applied Chemistry*, 87 (2015) 1051-1069.
- [220] J. Landers, G.Y. Gor, A.V. Neimark, Density functional theory methods for characterization of porous materials, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 437 (2013) 3-32.
- [221] P.I. Ravikovitch, G.L. Haller, A.V. Neimark, Density functional theory model for calculating pore size distributions: pore structure of nanoporous catalysts, *Advances in Colloid and Interface Science*, 76-77 (1998) 203-226.
- [222] A.H. Jadhav, G.M. Thorat, K. Lee, A.C. Lim, H. Kang, J.G. Seo, Effect of anion type of imidazolium based polymer supported ionic liquids on the solvent free synthesis of cycloaddition of CO₂ into epoxide, *Catalysis Today*, 265 (2016) 56-67.
- [223] J.A. Castro-Osma, J. Martínez, F. de la Cruz-Martínez, M.P. Caballero, J. Fernández-Baeza, J. Rodríguez-López, A. Otero, A. Lara-Sánchez, J. Tejeda, Development of hydroxy-containing imidazole organocatalysts for CO₂ fixation into cyclic carbonates, *Catalysis Science & Technology*, 8 (2018) 1981-1987.
- [224] F.D. Bobbink, P.J. Dyson, Synthesis of carbonates and related compounds incorporating CO₂ using ionic liquid-type catalysts: State-of-the-art and beyond, *Journal of Catalysis*, 343 (2016) 52-61.
- [225] P. Borowiecki, M. Milner-Krawczyk, J. Plenkiewicz, Chemoenzymatic synthesis and biological evaluation of enantiomerically enriched 1-(beta-hydroxypropyl)imidazolium- and triazolium-based ionic liquids, *Beilstein J Org Chem*, 9 (2013) 516-525.
- [226] A. Corma, H. Garcia, Lewis acids: from conventional homogeneous to green homogeneous and heterogeneous catalysis, *Chem Rev*, 103 (2003) 4307-4365.
- [227] M.J. Cordon, Consequences of the hydrophobicity and spatial constraints of confining environments in Lewis acid zeolites for aqueous-phase glucose isomerization catalysis, *Purdue University, West Lafayette, Indiana*, 2018, pp. 424.
- [228] T. Blasco, Synthesis, Characterization, and Catalytic Activity of Ti-MCM-41 Structures, *Journal of Catalysis*, 156 (1995) 65-74.
- [229] K. Lin, P. Pescarmona, H. Vandepitte, D. Liang, G. Vantendeloo, P. Jacobs, Synthesis and catalytic activity of Ti-MCM-41 nanoparticles with highly active titanium sites, *Journal of Catalysis*, 254 (2008) 64-70.
- [230] M. Guidotti, C. Pirovano, N. Ravasio, B. Lázaro, J.M. Fraile, J.A. Mayoral, B. Coq, A. Galarneau, The use of H₂O₂ over titanium-grafted mesoporous silica catalysts: a step further towards sustainable epoxidation, *Green Chemistry*, 11 (2009) 1421.
- [231] F. Bérubé, A. Khadhraoui, M.T. Janicke, F. Kleitz, S. Kaliaguine, Optimizing Silica Synthesis for the Preparation of Mesoporous Ti-SBA-15 Epoxidation Catalysts, *Industrial & Engineering Chemistry Research*, 49 (2010) 6977-6985.
- [232] B. Samran, S. Aungkutanont, T.J. White, S. Wongkasemjit, Room temperature synthesis of Ti-SBA-15 from silatrane and titanium-glycolate and its catalytic performance towards styrene epoxidation, *Journal of Sol-Gel Science and Technology*, 57 (2010) 221-228.
- [233] D.T. Bregante, A.M. Johnson, A.Y. Patel, E.Z. Ayla, M.J. Cordon, B.C. Bukowski, J. Greeley, R. Gounder, D.W. Flaherty, Cooperative Effects between Hydrophilic Pores and Solvents: Catalytic Consequences of Hydrogen Bonding on Alkene Epoxidation in Zeolites, *J Am Chem Soc*, 141 (2019) 7302-7319.
- [234] V. Smeets, C. Boissière, C. Sanchez, E.M. Gaigneaux, E. Peeters, B.F. Sels, M. Dusselier, D.P. Debecker, Aerosol Route to TiO₂-SiO₂ Catalysts with Tailored Pore Architecture and High Epoxidation Activity, *Chemistry of Materials*, 31 (2019) 1610-1619.
- [235] V. Smeets, E.M. Gaigneaux, D.P. Debecker, Hierarchical micro-/macroporous TS-1 zeolite epoxidation catalyst prepared by steam assisted crystallization, *Microporous and Mesoporous Materials*, 293 (2020).

- [236] M. Pitínová-Štekrová, P. Eliášová, T. Weissenberger, M. Shamzhy, Z. Musilová, J. Čejka, Highly selective synthesis of campholenic aldehyde over Ti-MWW catalysts by α -pinene oxide isomerization, *Catalysis Science & Technology*, 8 (2018) 4690-4701.
- [237] S. Ammaji, G.S. Rao, K.V.R. Chary, Acetalization of glycerol with acetone over various metal-modified SBA-15 catalysts, *Applied Petrochemical Research*, 8 (2018) 107-118.
- [238] M.J. Cordon, J.W. Harris, J.C. Vega-Vila, J.S. Bates, S. Kaur, M. Gupta, M.E. Witzke, E.C. Wegener, J.T. Miller, D.W. Flaherty, D.D. Hibbitts, R. Gounder, Dominant Role of Entropy in Stabilizing Sugar Isomerization Transition States within Hydrophobic Zeolite Pores, *J Am Chem Soc*, 140 (2018) 14244-14266.
- [239] W. Lueangchaichaweng, N.R. Brooks, S. Fiorilli, E. Gobechiya, K. Lin, L. Li, S. Parres-Esclapez, E. Javon, S. Bals, G. Van Tendeloo, J.A. Martens, C.E. Kirschhock, P.A. Jacobs, P.P. Pescarmona, Gallium oxide nanorods: novel, template-free synthesis and high catalytic activity in epoxidation reactions, *Angew Chem Int Ed Engl*, 53 (2014) 1585-1589.
- [240] B. Sorée, Synthèse de liquides ioniques supportés pour la conception de catalyseurs actifs dans la fixation chimique du dioxyde de carbone, Faculté des Sciences, Facultés Universitaires Notre-Dame de la Paix de Namur, Namur, 2012, pp. 86.
- [241] J. Kecht, A. Schlossbauer, T. Bein, Selective Functionalization of the Outer and Inner Surfaces in Mesoporous Silica Nanoparticles, *Chemistry of Materials*, 20 (2008) 7207-7214.
- [242] F. Carniato, C. Bisio, L. Sordelli, E. Gavrilova, M. Guidotti, Ti-POSS covalently immobilized onto mesoporous silica: A model for active sites in heterogeneous catalytic epoxidation, *Inorganica Chimica Acta*, 380 (2012) 244-251.
- [243] M. Guidotti, I. Batonneau-Gener, E. Gianotti, L. Marchese, S. Mignard, R. Psaro, M. Sgobba, N. Ravasio, The effect of silylation on titanium-containing silica catalysts for the epoxidation of functionalised molecules, *Microporous and Mesoporous Materials*, 111 (2008) 39-47.
- [244] M.S. Morey, S. O'Brien, S. Schwarz, G.D. Stucky, Hydrothermal and Postsynthesis Surface Modification of Cubic, MCM-48, and Ultralarge Pore SBA-15 Mesoporous Silica with Titanium, *Chemistry of Materials*, 12 (2000) 898-911.
- [245] I. Grohmann, W. Pilz, G. Walther, H. Kosslick, V.A. Tuan, XPS-investigation of titanium modified MFI-type zeolites, *Surface and Interface Analysis*, 22 (1994) 403-406.
- [246] Z. Luan, E.M. Maes, P.A.W. van der Heide, D. Zhao, R.S. Czernuszewicz, L. Kevan, Incorporation of Titanium into Mesoporous Silica Molecular Sieve SBA-15, *Chemistry of Materials*, 11 (1999) 3680-3686.
- [247] C. Liu, J. Huang, D. Sun, Y. Zhou, X. Jing, M. Du, H. Wang, Q. Li, Anatase type extra-framework titanium in TS-1: A vital factor influencing the catalytic activity toward styrene epoxidation, *Applied Catalysis A: General*, 459 (2013) 1-7.
- [248] A. Comès, S. Fiorilli, C. Aprile, Multifunctional heterogeneous catalysts highly performing in the conversion of carbon dioxide: Mechanistic insights, *Journal of CO2 Utilization*, 37 (2020) 213-221.
- [249] F. Schüth, M.D. Ward, J.M. Buriak, Common Pitfalls of Catalysis Manuscripts Submitted to *Chemistry of Materials*, *Chemistry of Materials*, 30 (2018) 3599-3600.
- [250] J. Liang, R.P. Chen, X.Y. Wang, T.T. Liu, X.S. Wang, Y.B. Huang, R. Cao, Postsynthetic ionization of an imidazole-containing metal-organic framework for the cycloaddition of carbon dioxide and epoxides, *Chem Sci*, 8 (2017) 1570-1575.
- [251] Z. Wang, K.J. Balkus, Synthesis and modification of titanium containing wrinkled mesoporous silica for cyclohexene epoxidation, *Microporous and Mesoporous Materials*, 243 (2017) 76-84.
- [252] J.-G. Wang, H. Wang, T. Yokoi, T. Tatsumi, Synthesis of Ti-containing extra-large-pore zeolites of Ti-CIT-5 and Ti-SSZ-53 and their catalytic applications, *Microporous and Mesoporous Materials*, 276 (2019) 207-212.
- [253] X. Ouyang, S.-J. Hwang, D. Xie, T. Rea, S.I. Zones, A. Katz, Heteroatom-Substituted Delaminated Zeolites as Solid Lewis Acid Catalysts, *ACS Catalysis*, 5 (2015) 3108-3119.

- [254] M. Fukuda, N. Tsunoji, Y. Yagenji, Y. Ide, S. Hayakawa, M. Sadakane, T. Sano, Highly active and selective Ti-incorporated porous silica catalysts derived from grafting of titanium(IV)acetylacetonate, *Journal of Materials Chemistry A*, 3 (2015) 15280-15291.
- [255] J. Silvestre-Alberó, M.E. Domine, J.L. Jordá, M.T. Navarro, F. Rey, F. Rodríguez-Reinoso, A. Corma, Spectroscopic, calorimetric, and catalytic evidences of hydrophobicity on Ti-MCM-41 silylated materials for olefin epoxidations, *Applied Catalysis A: General*, 507 (2015) 14-25.
- [256] R. Srivastava, D. Srinivas, P. Ratnasamy, CO₂ activation and synthesis of cyclic carbonates and alkyl/aryl carbamates over adenine-modified Ti-SBA-15 solid catalysts, *Journal of Catalysis*, 233 (2005) 1-15.
- [257] R. Srivastava, D. Srinivas, P. Ratnasamy, Sites for CO₂ activation over amine-functionalized mesoporous Ti(Al)-SBA-15 catalysts, *Microporous and Mesoporous Materials*, 90 (2006) 314-326.
- [258] Y.L. Hu, H.B. Wang, Z.W. Chen, X.G. Li, Titanium Incorporated Mesoporous Silica Immobilized Functional Ionic Liquid as an Efficient Reusable Catalyst for Cycloaddition of Carbon Dioxide to Epoxides, *ChemistrySelect*, 3 (2018) 5087-5091.
- [259] W.-L. Dai, L. Chen, S.-F. Yin, S.-L. Luo, C.-T. Au, 3-(2-Hydroxyl-Ethyl)-1-Propylimidazolium Bromide Immobilized on SBA-15 as Efficient Catalyst for the Synthesis of Cyclic Carbonates via the Coupling of Carbon Dioxide with Epoxides, *Catalysis Letters*, 135 (2010) 295-304.
- [260] B.M. Bhanage, S.-I. Fujita, Y. Ikushima, M. Arai, Synthesis of dimethyl carbonate and glycols from carbon dioxide, epoxides, and methanol using heterogeneous basic metal oxide catalysts with high activity and selectivity, *Applied Catalysis A: General*, 219 (2001) 259-266.
- [261] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, Mg-Al Mixed Oxides as Highly Active Acid-Base Catalysts for Cycloaddition of Carbon Dioxide to Epoxides, *Journal of the American Chemical Society*, 121 (1999) 4526-4527.
- [262] E.J. Dorskocil, Ion-exchanged ETS-10 catalysts for the cycloaddition of carbon dioxide to propylene oxide, *Microporous and Mesoporous Materials*, 76 (2004) 177-183.
- [263] E.J. Dorskocil, Effect of water and alkali modifications on ETS-10 for the cycloaddition of CO₂ to propylene oxide, *J Phys Chem B*, 109 (2005) 2315-2320.
- [264] R.B. Borade, A. Clearfield, Synthesis of aluminum rich MCM-41, *Catalysis Letters*, 31 (1995) 267-272.
- [265] K.R. Kloetstra, H.W. Zandbergen, H. van Bekkum, MCM-41 type materials with low Si/Al ratios, *Catalysis Letters*, 33 (1995) 157-163.
- [266] J. Chen, T. Chen, N. Guan, J. Wang, Dealumination process of zeolite omega monitored by ²⁷Al 3QMAS NMR spectroscopy, *Catalysis Today*, 93-95 (2004) 627-630.
- [267] S. Li, A. Zheng, Y. Su, H. Fang, W. Shen, Z. Yu, L. Chen, F. Deng, Extra-framework aluminium species in hydrated faujasite zeolite as investigated by two-dimensional solid-state NMR spectroscopy and theoretical calculations, *Physical chemistry chemical physics : PCCP*, 12 (2010) 3895-3903.
- [268] E. Rombi, M.G. Cutrufello, C. Cannas, M. Occhiuzzi, B. Onida, I. Ferino, Gold-assisted E' centres formation on the silica surface of Au/SBA-15 catalysts for low temperature CO oxidation, *Physical chemistry chemical physics : PCCP*, 14 (2012) 6889-6897.
- [269] S. Varghese, M.G. Cutrufello, E. Rombi, R. Monaci, C. Cannas, I. Ferino, Mesoporous hard-templated Me-Co [Me = Cu, Fe] spinel oxides for water gas shift reaction, *Journal of Porous Materials*, 21 (2014) 539-549.
- [270] L. Atzori, M.G. Cutrufello, D. Meloni, R. Monaci, C. Cannas, D. Gazzoli, M.F. Sini, P. Deiana, E. Rombi, CO₂ methanation on hard-templated NiO CeO₂ mixed oxides, *International Journal of Hydrogen Energy*, 42 (2017) 20689-20702.
- [271] M. Imperor-Clerc, D. Bazin, M.-D. Appay, P. Beaunier, A. Davidson, Crystallization of β -MnO₂Nanowires in the Pores of SBA-15 Silicas: In Situ Investigation Using Synchrotron Radiation, *Chemistry of Materials*, 16 (2004) 1813-1821.
- [272] M. Mureddu, I. Ferino, E. Rombi, M.G. Cutrufello, P. Deiana, A. Ardu, A. Musinu, G. Piccaluga, C. Cannas, ZnO/SBA-15 composites for mid-temperature removal of H₂S: Synthesis, performance and regeneration studies, *Fuel*, 102 (2012) 691-700.

- [273] C. Calabrese, L. Fusaro, L.F. Liotta, F. Giacalone, A. Comès, V. Campisciano, C. Aprile, M. Gruttadauria, Efficient Conversion of Carbon Dioxide by Imidazolium-Based Cross-Linked Nanostructures Containing Polyhedral Oligomeric Silsesquioxane (POSS) Building Blocks, *ChemPlusChem*, 84 (2019) 1536-1543.
- [274] A. Ungureanu, B. Dragoi, V. Hulea, T. Cacciaguerra, D. Meloni, V. Solinas, E. Dumitriu, Effect of aluminium incorporation by the "pH-adjusting" method on the structural, acidic and catalytic properties of mesoporous SBA-15, *Microporous and Mesoporous Materials*, 163 (2012) 51-64.
- [275] A. Corma, H. García, Lewis Acids: From Conventional Homogeneous to Green Homogeneous and Heterogeneous Catalysis, *Chemical Reviews*, 103 (2003) 4307-4365.
- [276] U. Mayer, V. Gutmann, W. Gerger, The Acceptor Number -- A Quantitative Empirical Parameter for the Electrophilic Properties of Solvents, *Monatshefte für Chemie*, 106 (1975) 1235-1257.
- [277] M. Beckett, G. Strickland, J. Holland, K. Varma, A convenient n.m.r method for the measurement of Lewis acidity at boron centres: correlation of reaction rates of Lewis acid initiated epoxide polymerizations with Lewis acidity, *Polymer communications*, 37 (1996) 4629-4631.
- [278] M. Metz, D. Schwartz, C. Stern, T. Marks, P. Nickias, New Perfluoroarylborane Activators for Single-Site Olefin Polymerization. Acidity and Cocatalytic Properties of a "Superacidic" Perfluorodiboranthracene, *Organometallics*, 21 (2002) 4159-4168.
- [279] S. Kobayashi, T. Busujima, S. Nagayama, A Novel Classification of Lewis Acids on the Basis of Activity and Selectivity, *Chemistry: A European Journal*, 6 (2000) 3491-3494.
- [280] C. Branch, S. Bott, A. Barron, Group 13 trihalide complexes of 9-fluorenone: a comparison of methods for assigning relative Lewis acidity, *Journal of Organometallic Chemistry*, 666 (2003) 23-34.
- [281] L. Greb, LewisSuperacids:Classifications, Candidates, and Applications, *Chemistry: A European Journal*, 24 (2018) 17881 -17896.
- [282] I. Sivaev, V. Bregadze, Lewis acidity of boron compounds, *Coordination Chemistry Reviews*, 270-271 (2014) 75-88.
- [283] K. Kucinski, G. Hreczycho, Chemoselective and Catalyst-Free O-Borylation of Silanols: A Facile Access to Borasiloxanes, *ChemSusChem*, 10 (2017) 4695-4698.
- [284] J. Kazmierczak, K. Kucinski, H. Stachowiak, G. Hreczycho, Introduction of Boron Functionalities into Silsesquioxanes: Novel Independent Methodologies, *Chemistry*, 24 (2018) 2509-2514.
- [285] S. Kisan, V. Krishnakumar, C. Gunanathan, Ruthenium-Catalyzed Anti-Markovnikov Selective Hydroboration of Olefins, *ACS Catalysis*, 7 (2017) 5950-5954.
- [286] Y.J. Wanglee, J. Hu, R.E. White, M.Y. Lee, S.M. Stewart, P. Perrotin, S.L. Scott, Borane-induced dehydration of silica and the ensuing water-catalyzed grafting of B(C₆F₅)₃ to give a supported, single-site Lewis acid, identical with SiOB(C₆F₅)₂, *J Am Chem Soc*, 134 (2012) 355-366.
- [287] C. Cossement, J. Darville, J.-M. Gilles, J.B. Nagy, C. Fernandez, J.-P. Amoureux, Chemical shift anisotropy and indirect coupling in SnO₂ and SnO, *Magnetic Resonance in Chemistry*, 30 (1992) 263-270.